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(US). MAWSON, Simon; 318 South Pointe, Charleston, WV 25314 (US). KWACK, Tae, Hoon; 241 Berkley Avenue, Belle Mead, NJ 08502 (US). KAROL, Frederick, J.; 157 Skyline Drive, Lakewood, NJ 08701 (US). SCHRECK, David, James; 5226 Sun Valley Drive, Cross Lanes, WV 25313 (US). GOODE, Mark, G.; 17 Meadowbrook Circle, Hurricane, WV 25526 (US). DANIELL, Paul, T.; 147 Edge Water Lane, Tornado, WV 25202 (US). MCKEE, Matthew, G.; 3508 Noyes Avenue, Apt. B, Charleston, WV 25304 (US). WILLIAMS, Clark, C.; 1105 Skytop Circle, Charleston, WV 25314 (US).

(74) Agents: SHER, Jaimes et al.; Univation Technologies, LLC, 5555 San Felipe, Suite 1950, Houston, TX 77056 (US).

(81) Designated States (*national*): AU, BR, BY, CA, CN, CZ, ID, IL, IN, JP, KR, MX, NO, PL, RU, SG, SK, TR, ZA.

(71) Applicant: UNIVATION TECHNOLOGIES, LLC [US/US]; Suite 1950, 5555 San Felipe, Houston, TX 77056 (US).

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(72) Inventors: MCCONVILLE, David, H.; 4015 Cinnamon Fern Court, Houston, TX 77059 (US). LOVEDAY, Donald, R.; 2419 Jasmine Ridge Court, Houston, TX 77062 (US). HOLT CAMP, Matthew, W.; 26935 Carol Drive, Huffman, TX 77336 (US). SZUL, John, F.; 5 Lake Lane, Nitro, WV 25143 (US). ERICKSON, Kersten, Anne; 825-A, Glendale Avenue, South Charleston, WV 25303

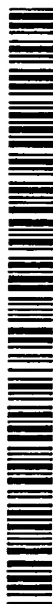
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(54) Title: CATALYST COMPOSITIONS, METHODS OF POLYMERIZATION, AND POLYMERS THEREFROM

(57) Abstract: The present invention provides catalyst compositions useful in polymerization processes, including a Group 15 containing metal compound, mixed catalyst compositions including the Group 15 containing metal compound and a second metal compound which is preferably a bulky ligand metallocene catalyst, supported and unsupported catalyst systems thereof, and a process for polymerizing olefin(s) utilizing them. The invention also discloses a new polyolefin, generally polyethylene, particularly a multimodal polymer and more specifically, a bimodal polymer, and its use in various end-use applications such as film, molding and pipe.



WO 01/30861 A1

**CATALYST COMPOSITIONS, METHODS OF
POLYMERIZATION, AND POLYMERS THEREFROM**

5 FIELD OF THE INVENTION

The present invention relates to a catalyst composition including a Group 15 containing metal compound, and to a mixed catalyst composition including at least two metal compounds. Preferably, at least one of the metal compounds of the mixed composition is the Group 15 containing metal compound. More preferably, the other metal compound is a bulky ligand metallocene catalyst compound. The present invention also relates to catalyst systems utilizing the catalyst compositions, and to their use in olefin(s) polymerization. The present invention further relates to a new polyolefin, generally polyethylene, particularly a multimodal polymer and more specifically, a bimodal polymer, and its use in various end-use applications such as film, molding and pipe.

15 BACKGROUND OF THE INVENTION

Advances in polymerization and catalysis have resulted in the capability to produce many new polymers having improved physical and chemical properties useful in a wide variety of superior products and applications. With the development of new catalysts, the choice of polymerization-type (solution, slurry, high pressure or gas phase), for producing a particular polymer, has been greatly expanded. Also, advances in polymerization technology have provided more efficient, highly productive and economically enhanced processes. Especially illustrative of these advances is the development of technology utilizing bulky ligand metallocene catalyst systems.

25 More recently, developments have lead to the discovery of anionic, multidentate heteroatom ligands as discussed by the following articles: (1) Kempe et al., "Aminopyridinato Ligands - New Directions and Limitations", 80th Canadian Society for Chemistry Meeting, Windsor, Ontario, Canada, June 1-4, 1997; (2) Kempe et al., *Inorg. Chem.* 1996 vol 35 6742; (3) Jordan *et al.* of polyolefin catalysts based on hydroxyquinolines
30 (Bei, X.; Swenson, D. C.; Jordan, R. F., *Organometallics* 1997, 16, 3282); (4) Horton, et.al., "Cationic Alkylzirconium Complexes Based on a Tridentate Diamide Ligand: New Alkene Polymerization Catalysts", *Organometallics*, 1996, 15, 2672-2674 relates to tridentate

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zirconium complexes; (5) Baumann, et al., "Synthesis of Titanium and Zirconium Complexes that Contain the Tridentate Diamido Ligand $[(t\text{-Bu-d}_6\text{N-O-C}_6\text{H}_4)_2\text{O}]^{2-}\{[\text{NON}]^{2-}\}$ and the Living Polymerization of 1-Hexene by Activated $[\text{NON}]\text{ZrMe}_2$ ", Journal of the American Chemical Society, Vol. 119, pp. 3830-3831; (6) Cloke et al., "Zirconium Complexes incorporating the New Tridentate Diamide Ligand $[(\text{Me}_3\text{Si})\text{N}\{\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)_2\}]^{2-}(\text{L})$; the Crystal Structure of $[\text{Zr}(\text{BH}_4)_2\text{L}]$ and $[\text{ZrCl}\{\text{CH}(\text{SiMe}_3)_2\}\text{L}]$ ", J. Chem. Soc. Dalton Trans, pp. 25-30, 1995; (7) Clark et al., "Titanium (IV) complexes incorporating the aminodiamide ligand $[(\text{SiMe}_3)\text{N}\{\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)_2\}]^{2-}(\text{L})$; the X-ray crystal structure of $[\text{TiMe}_2(\text{L})]$ and $[\text{TiCl}\{\text{CH}(\text{SiMe}_3)_2\}(\text{L})]$ ", Journal of Organometallic Chemistry, Vol 50, pp. 333-340, 1995; (8) Scollard et al., "Living Polymerization of alpha-olefins by Chelating Diamide Complexes of Titanium", J. Am. Chem. Soc., Vol 118, No. 41, pp. 10008-10009, 1996; and (9) Guerin et al., "Conformationally Rigid Diamide Complexes: Synthesis and Structure of Titanium (IV) Alkyl Derivatives", Organometallics, Vol 15, No. 24, pp. 5085-5089, 1996.

Furthermore, U.S. Patent No. 5,576,460 describes a preparation of arylamine ligands and U.S. Patent No. 5,889,128 discloses a process for the living polymerization of olefins using initiators having a metal atom and a ligand having two group 15 atoms and a group 16 atom or three group 15 atoms. EP 893 454 A1 also describes preferably titanium transition metal amide compounds. In addition, U.S. Patent No. 5,318,935 discusses amido transition metal compounds and catalyst systems especially for the producing isotactic polypropylene. Polymerization catalysts containing bidentate and tridentate ligands are further discussed in U.S. Patent No. 5,506,184.

Traditional bulky ligand metallocene catalyst systems produce polymers that are in some situations more difficult to process into film, for example using old extrusion equipment. One technique to improve these polymers is to blend them with other polymers with the intent to create a blend having the desired properties that each component individually would have. While the two polymer blends tend to be more processable, it is expensive and adds a cumbersome blending step to the manufacturing/fabrication process.

Higher molecular weight confers desirable polymer mechanical properties and stable bubble formation in the production of films. However, this property also inhibits extrusion processing by increasing backpressure in extruders, promotes melt fracture defects in the inflating bubble and potentially, promotes too high a degree of orientation in the finished film. The anionic, multidentate heteroatom containing catalyst systems tend to produce a

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very high molecular weight polymer. To remedy this, one may form a secondary, minor component of lower molecular weight polymer to reduce extruder backpressure and inhibit melt fracture. Several industrial processes operate on this principle using multiple reactor technology to produce a processable bimodal molecular weight distribution (MWD) high density polyethylene (HDPE) product. HIZEX™, a Mitsui Chemicals HDPE product, is considered the worldwide standard. HIZEX™ is produced in a costly two or more reactor process. In a multiple reactor process, each reactor produces a single component of the final product.

Others in the art have tried to produce two polymers together at the same time in the same reactor using two different catalysts. PCT patent application WO 99/03899 discloses using a typical bulky ligand metallocene catalyst and a conventional-type Ziegler-Natta catalyst in the same reactor to produce a bimodal polyolefin. Using two different types of catalysts, however, result in a polymer whose characteristics cannot be predicted from those of the polymers that each catalyst would produce if utilized separately. This unpredictability occurs, for example, from competition or other influence between the catalyst or catalyst systems used.

Polyethylenes with a higher density and a higher molecular weight are valued in film applications requiring high stiffness, good toughness and high throughput. Such polymers are also valued in pipe applications requiring stiffness, toughness and long-term durability, and particularly resistance to environmental stress cracking.

Thus, there is a desire for an improved catalyst compound and for a combination of catalysts capable of producing processable polyethylene polymers, preferably in a single reactor having desirable combinations of processing, mechanical and optical properties.

Summary of the Invention

The present invention provides for catalyst compounds, catalyst systems, and mixed catalyst systems, and for their use in polymerization processes, polymers produced therefrom, and products made from the polymer.

In one embodiment, the invention is directed to a catalyst compound including a Group 15 containing metal compound, and to a mixed catalyst composition including at least two metal compounds, where at least one metal compound of the mixed composition is the Group 15 containing metal compound, and where the other metal compound is a bulky ligand metallocene compound, a conventional transition metal catalyst, or combinations thereof, to

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catalyst systems including these catalysts, to their use in olefin(s) polymerization and to polymers made therefrom.

In another embodiment, the invention is directed to a Group 15 containing bidentate or tridentate ligated Group 3 to 14 metal compound, preferably a Group 3 to 7, more preferably a Group 4 to 6, and even more preferably a Group 4 metal catalyst compound, and to a mixed catalyst composition including at least two metal compounds, where at least one metal compound is the Group 15 containing catalyst compound described above, and where the other metal compound is a bulky ligand metallocene compound, a conventional transition metal catalyst, or combinations thereof, to catalyst systems including these catalysts, to their use in olefin(s) polymerization and to polymers made therefrom.. In this embodiment it is preferred that the other metal compound is a bulky ligand metallocene compound.

In another embodiment, the invention is directed to a Group 3 to 14 metal atom bound to at least one leaving group and also bound to at least two Group 15 atoms, at least one of which is also bound to a Group 15 or 16 atom through another group catalyst compound, and to a mixed catalyst composition including at least two metal compounds, where one metal compound is the Group 15 containing catalyst compound described above, and where the second metal compound, is different from the first metal compound, and is a bulky ligand metallocene catalyst, a conventional-type transition metal catalyst, or combinations thereof, to catalyst systems including these catalysts, to their use in olefin(s) polymerization and to polymers made therefrom..

In another embodiment, the invention is directed to a method of supporting the catalysts compositions described herein, to the supported catalyst systems themselves, and to their use in olefin(s) polymerization.

In another embodiment, the invention is directed to the use of a Lewis acid aluminum containing activator with the catalyst compositions and systems described herein.

In another embodiment, the invention is directed to a method of feeding the catalyst compositions and systems described herein into a polymerization reactor in a liquid carrier.

In another embodiment, the invention is directed to a process for polymerizing olefin(s), particularly in a gas phase or slurry phase process, utilizing any one of the catalyst systems or supported catalyst systems described herein.

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In another embodiment, the invention is directed to processes for polymerizing olefin(s) utilizing the mixed catalyst compositions described above, especially in a single polymerization reactor. More preferably, the process utilizes a continuous gas phase single reactor process producing a multimodal polymer.

5 In another embodiment, the invention is directed to the polymers prepared utilizing the above mixed catalyst composition, and preferably to a new bimodal MWD HDPE.

BRIEF DESCRIPTION OF THE DRAWINGS:

Figure 1 is a graphic representation of Illustration 1 below.
10 Figure 2 is a graphic representation of Illustration 2 below.
Figure 3 is a graphic representation of Illustration 3 below.
Figure 4 is a graphic representation of Illustration 4 below.
Figure 5 is a graphic representation of Illustration 5 below.
Figure 6 is a graphic representation of Illustration 6 below.
15 Figure 7 is a graphic representation of Illustration 7 below.
Figure 8 is a graphic representation of Illustration 8 below.
Figure 9 is a graphic representation of Illustration 9 below.

DETAILED DESCRIPTION OF THE INVENTION

20

Introduction

The present invention relates to the use of a Group 15 containing metal catalyst compound in olefin(s) polymerization. In addition, Applicants have discovered that using these Group 15 containing catalyst compounds, in combination with another catalyst,
25 preferably a bulky ligand metallocene compound, produces a new bimodal MWD HDPE product. Surprisingly, the mixed catalyst composition of the present invention may be utilized in a single reactor system.

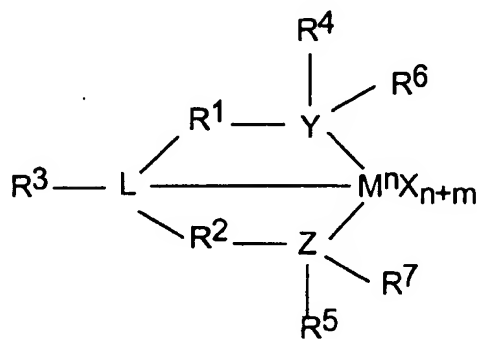
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Group 15 Containing Metal Compound

The Group 15 containing compound generally includes a Group 3 to 14 metal atom, preferably a Group 3 to 7, more preferably a Group 4 to 6, and even more preferably a Group 4 metal atom, bound to at least one leaving group and also bound to at least two Group 15 atoms, at least one of which is also bound to a Group 15 or 16 atom through another group.

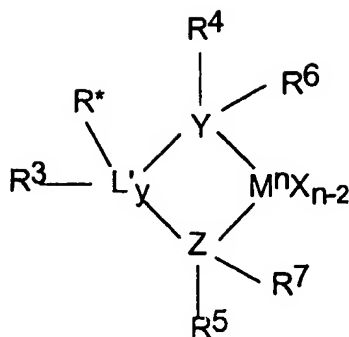
In one embodiment, at least one of the Group 15 atoms is also bound to a Group 15 or 16 atom through another group which may be a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead, or phosphorus, wherein the Group 15 or 16 atom may also be bound to nothing or a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group, and wherein each of the two Group 15 atoms are also bound to a cyclic group and may optionally be bound to hydrogen, a halogen, a heteroatom or a hydrocarbyl group, or a heteroatom containing group.

In another embodiment, the Group 15 containing metal compound of the present invention may be represented by the formulae:



Formula I or

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Formula II

5 wherein

M is a Group 3 to 12 transition metal or a Group 13 or 14 main group metal, preferably a Group 4, 5, or 6 metal, and more preferably a Group 4 metal, and most preferably zirconium, titanium or hafnium,

10 each X is independently a leaving group, preferably, an anionic leaving group, and more preferably hydrogen, a hydrocarbyl group, a heteroatom or a halogen, and most preferably an alkyl.

y is 0 or 1 (when y is 0 group L' is absent),

n is the oxidation state of M, preferably +3, +4, or +5, and more preferably +4,

15 m is the formal charge of the YZL or the YZL' ligand, preferably 0, -1, -2 or -3, and more preferably -2,

L is a Group 15 or 16 element, preferably nitrogen,

L' is a Group 15 or 16 element or Group 14 containing group, preferably carbon, silicon or germanium,

Y is a Group 15 element, preferably nitrogen or phosphorus, and more preferably nitrogen,

20 Z is a Group 15 element, preferably nitrogen or phosphorus, and more preferably nitrogen,

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus, preferably a C₂ to C₂₀ alkyl, aryl or aralkyl group, more preferably a linear, branched or cyclic C₂ to C₂₀ alkyl group, most preferably a C₂ to C₆ hydrocarbon group.

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R^3 is absent or a hydrocarbon group, hydrogen, a halogen, a heteroatom containing group, preferably a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms, more preferably R^3 is absent, hydrogen or an alkyl group, and most preferably hydrogen

R^4 and R^5 are independently an alkyl group, an aryl group, substituted aryl group, a cyclic

5 alkyl group, a substituted cyclic alkyl group, a cyclic aralkyl group, a substituted cyclic aralkyl group or multiple ring system, preferably having up to 20 carbon atoms, more preferably between 3 and 10 carbon atoms, and even more preferably a C_1 to C_{20} hydrocarbon group, a C_1 to C_{20} aryl group or a C_1 to C_{20} aralkyl group, or a heteroatom containing group, for example PR_3 , where R is an alkyl group,

10 R^1 and R^2 may be interconnected to each other, and/or R^4 and R^5 may be interconnected to each other,

R^6 and R^7 are independently absent, or hydrogen, an alkyl group, halogen, heteroatom or a hydrocarbyl group, preferably a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms, more preferably absent, and

15 R^* is absent, or is hydrogen, a Group 14 atom containing group, a halogen, a heteroatom containing group.

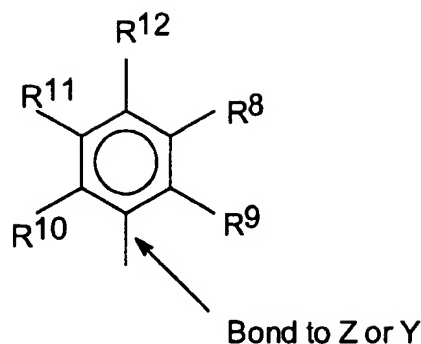
By "formal charge of the YZL or YZL' ligand", it is meant the charge of the entire ligand absent the metal and the leaving groups X.

By " R^1 and R^2 may also be interconnected" it is meant that R^1 and R^2 may be directly
20 bound to each other or may be bound to each other through other groups. By " R^4 and R^5 may also be interconnected" it is meant that R^4 and R^5 may be directly bound to each other or may be bound to each other through other groups.

An alkyl group may be a linear, branched alkyl radicals, or alkenyl radicals, alkynyl radicals, cycloalkyl radicals or aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals,
25 aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxy carbonyl radicals, carbomoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. An aralkyl group is defined to be a substituted aryl group.

In a preferred embodiment R^4 and R^5 are independently a group represented by the
30 following formula:

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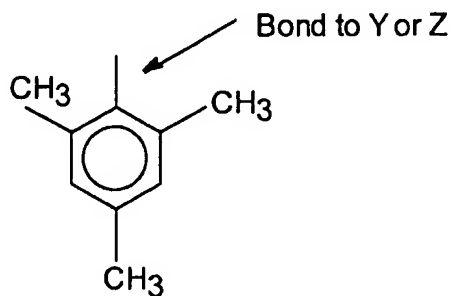
Formula 1

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wherein

R⁸ to R¹² are each independently hydrogen, a C₁ to C₄₀ alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms, preferably a C₁ to C₂₀ linear or branched alkyl group, preferably a methyl, ethyl, propyl or butyl group, any two R groups
 10 may form a cyclic group and/or a heterocyclic group. The cyclic groups may be aromatic. In a preferred embodiment R⁹, R¹⁰ and R¹² are independently a methyl, ethyl, propyl or butyl group (including all isomers), in a preferred embodiment R⁹, R¹⁰ and R¹² are methyl groups, and R⁸ and R¹¹ are hydrogen.

In a particularly preferred embodiment R⁴ and R⁵ are both a group represented by the
 15 following formula:



Formula 2

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In this embodiment, M is a Group 4 metal, preferably zirconium, titanium or hafnium, and even more preferably zirconium; each of L, Y, and Z is nitrogen; each of R¹ and R² is -CH₂-CH₂-; R³ is hydrogen; and R⁶ and R⁷ are absent.

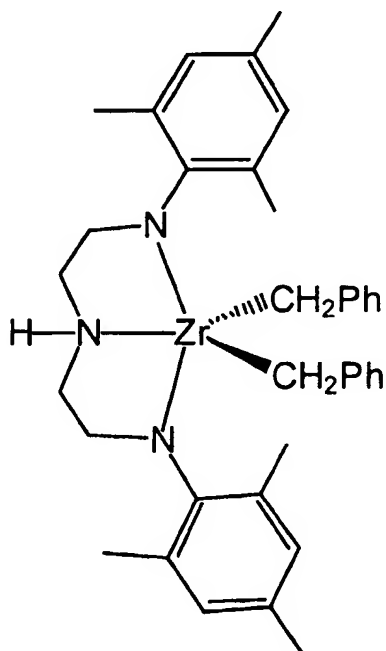
In a preferred embodiment, at least one X is a substituted hydrocarbon group, preferably a substituted alkyl group having more than 6 carbon atoms, most preferably an aryl substituted alkyl group. The most preferably aryl substituted alkyl group is benzyl.

In a particularly preferred embodiment the Group 15 containing metal compound is represented by the formula:

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Compound I

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In compound I, Ph equals phenyl.

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The Group 15 containing metal compounds of the invention are prepared by methods known in the art, such as those disclosed in EP 0 893 454 A1, U.S. Patent No. 5,889,128 and the references cited in U.S. Patent No. 5,889,128 which are all herein incorporated by reference. U.S. Application Serial Number 09/312,878, filed May 17, 1999, discloses a gas

or slurry phase polymerization process using a supported bisamide catalyst, which is also incorporated herein by reference.

A preferred direct synthesis of these compounds comprises reacting the neutral ligand, (see for example YZL or YZL' of formula I or II) with M^nX_n (M is a Group 3 to 14 metal, n is the oxidation state of M, each X is an anionic group, such as halide, in a non-coordinating or weakly coordinating solvent, such as ether, toluene, xylene, benzene, methylene chloride, and/or hexane or other solvent having a boiling point above 60 °C, at about 20 to about 150 °C (preferably 20 to 100 °C), preferably for 24 hours or more, then treating the mixture with an excess (such as four or more equivalents) of an alkylating agent, such as methyl magnesium bromide in ether. The magnesium salts are removed by filtration, and the metal complex isolated by standard techniques.

In one embodiment the Group 15 containing metal compound is prepared by a method comprising reacting a neutral ligand, (see for example YZL or YZL' of formula 1 or 2) with a compound represented by the formula M^nX_n (where M is a Group 3 to 14 metal, n is the oxidation state of M, each X is an anionic leaving group) in a non-coordinating or weakly coordinating solvent, at about 20 °C or above, preferably at about 20 to about 100 °C, then treating the mixture with an excess of an alkylating agent, then recovering the metal complex. In a preferred embodiment the solvent has a boiling point above 60 °C, such as toluene, xylene, benzene, and/or hexane. In another embodiment the solvent comprises ether and/or methylene chloride, either being preferable.

Bulky Ligand Metallocene Compound

In one embodiment, the Group 15 containing metal compound described above may be combined with a second metal compound to form a mixed catalyst composition. The second metal compound is preferably a bulky ligand metallocene compound.

Generally, bulky ligand metallocene compounds include half and full sandwich compounds having one or more bulky ligands bonded to at least one metal atom. Typical bulky ligand metallocene compounds are generally described as containing one or more bulky ligand(s) and one or more leaving group(s) bonded to at least one metal atom. In one

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preferred embodiment, at least one bulky ligands is η -bonded to the metal atom, most preferably η^5 -bonded to the metal atom.

The bulky ligands are generally represented by one or more open, acyclic, or fused ring(s) or ring system(s) or a combination thereof. These bulky ligands, preferably the ring(s) or ring system(s) are typically composed of atoms selected from Groups 13 to 16 atoms of the Periodic Table of Elements, preferably the atoms are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum or a combination thereof. Most preferably the ring(s) or ring system(s) are composed of carbon atoms such as but not limited to those cyclopentadienyl ligands or cyclopentadienyl-type ligand structures or other similar functioning ligand structure such as a pentadiene, a cyclooctatetraendiyl or an imide ligand. The metal atom is preferably selected from Groups 3 through 15 and the lanthanide or actinide series of the Periodic Table of Elements. Preferably the metal is a transition metal from Groups 4 through 12, more preferably Groups 4, 5 and 6, and most preferably the transition metal is from Group 4.

In one embodiment, the bulky ligand metallocene catalyst compounds are represented by the formula:



where M is a metal atom from the Periodic Table of the Elements and may be a Group 3 to 12 metal or from the lanthanide or actinide series of the Periodic Table of Elements, preferably M is a Group 4, 5 or 6 transition metal, more preferably M is a Group 4 transition metal, even more preferably M is zirconium, hafnium or titanium. The bulky ligands, L^A and L^B , are open, acyclic or fused ring(s) or ring system(s) and are any ancillary ligand system, including unsubstituted or substituted, cyclopentadienyl ligands or cyclopentadienyl-type ligands, heteroatom substituted and/or heteroatom containing cyclopentadienyl-type ligands. Non-limiting examples of bulky ligands include cyclopentadienyl ligands, cyclopentaphenanthrenyl ligands, indenyl ligands, benzindenyl ligands, fluorenyl ligands, octahydrofluorenyl ligands, cyclooctatetraendiyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, phosphinimine (WO 99/40125), pyrrolyl ligands, pyrozoilyl ligands, carbazoyl ligands, borabenzene ligands and the like, including hydrogenated versions thereof, for example tetrahydroindenyl ligands. In one embodiment, L^A and L^B may be any other ligand structure capable of η -bonding to M, preferably η^3 -bonding to M and most preferably η^5 -bonding. In yet another embodiment,

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the atomic molecular weight (MW) of L^A or L^B exceeds 60 a.m.u., preferably greater than 65 a.m.u.. In another embodiment, L^A and L^B may comprise one or more heteroatoms, for example, nitrogen, silicon, boron, germanium, sulfur and phosphorous, in combination with carbon atoms to form an open, acyclic, or preferably a fused, ring or ring system, for example, a hetero-cyclopentadienyl ancillary ligand. Other L^A and L^B bulky ligands include but are not limited to bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borollides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles. Independently, each L^A and L^B may be the same or different type of bulky ligand that is bonded to M. In one embodiment of formula (III) only one of either L^A or L^B is present.

Independently, each L^A and L^B may be unsubstituted or substituted with a combination of substituent groups R. Non-limiting examples of substituent groups R include one or more from the group selected from hydrogen, or linear, branched alkyl radicals, or alkenyl radicals, alkynyl radicals, cycloalkyl radicals or aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxy carbonyl radicals, carbomoyl radicals, alkyl- or dialkyl-carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. In a preferred embodiment, substituent groups R have up to 50 non-hydrogen atoms, preferably from 1 to 30 carbon, that can also be substituted with halogens or heteroatoms or the like. Non-limiting examples of alkyl substituents R include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers, for example tertiary butyl, isopropyl, and the like. Other hydrocarbyl radicals include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl, chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)-silyl, methyl-bis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Non-hydrogen substituents R include the atoms carbon, silicon, boron, aluminum, nitrogen, phosphorous, oxygen, tin, sulfur, germanium and the like, including olefins such as but not limited to olefinically unsaturated substituents including vinyl-terminated ligands, for example but-3-enyl, prop-2-enyl, hex-5-enyl and the like. Also, at least two R groups, preferably two adjacent R groups, are joined to form a ring structure having from 3 to 30 atoms selected from carbon, nitrogen, oxygen, phosphorous, silicon,

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germanium, aluminum, boron or a combination thereof. Also, a substituent group R group such as 1-butanyl may form a carbon sigma bond to the metal M.

Other ligands may be bonded to the metal M, such as at least one leaving group Q. In one embodiment, Q is a monoanionic labile ligand having a sigma-bond to M. Depending on the oxidation state of the metal, the value for n is 0, 1 or 2 such that formula (III) above represents a neutral bulky ligand metallocene catalyst compound.

Non-limiting examples of Q ligands include weak bases such as amines, phosphines, ethers, carboxylates, dienes, hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides or halogens and the like or a combination thereof. In another embodiment, two or more Q's form a part of a fused ring or ring system. Other examples of Q ligands include those substituents for R as described above and including cyclobutyl, cyclohexyl, heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methylenide, methoxy, ethoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, dimethylphosphide radicals and the like.

In one embodiment, the bulky ligand metallocene catalyst compounds of the invention include those of formula (III) where L^A and L^B are bridged to each other by at least one bridging group, A, such that the formula is represented by



These bridged compounds represented by formula (IV) are known as bridged, bulky ligand metallocene catalyst compounds. L^A , L^B , M, Q and n are as defined above. Non-limiting examples of bridging group A include bridging groups containing at least one Group 13 to 16 atom, often referred to as a divalent moiety such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom or a combination thereof. Preferably bridging group A contains a carbon, silicon or germanium atom, most preferably A contains at least one silicon atom or at least one carbon atom. The bridging group A may also contain substituent groups R as defined above including halogens and iron. Non-limiting examples of bridging group A may be represented by R'_2C , R'_2Si , $R'_2Si R'_2Si$, R'_2Ge , R'_2P , where R' is independently, a radical group which is hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen or two or more R' may be joined to form a ring or ring system. In one embodiment, the bridged, bulky ligand metallocene catalyst compounds of formula (IV) have two or more bridging groups A (EP 664 301 B1).

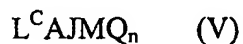
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In one embodiment, the bulky ligand metallocene catalyst compounds are those where the R substituents on the bulky ligands L^A and L^B of formulas (III) and (IV) are substituted with the same or different number of substituents on each of the bulky ligands. In another embodiment, the bulky ligands L^A and L^B of formulas (III) and (IV) are different from each other.

Other bulky ligand metallocene catalyst compounds and catalyst systems useful in the invention may include those described in U.S. Patent Nos. 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031, 5,304,614, 5,677,401, 5,723,398, 5,753,578, 5,854,363, 5,856,547, 5,858,903, 5,859,158, 5,900,517 and 5,939,503 and PCT publications WO 93/08221, WO 93/08199, WO 95/07140, WO 98/11144, WO 98/41530, WO 98/41529, WO 98/46650, WO 99/02540 and WO 99/14221 and European publications EP-A-0 578 838, EP-A-0 638 595, EP-B-0 513 380, EP-A1-0 816 372, EP-A2-0 839 834, EP-B1-0 632 819, EP-B1-0 748 821 and EP-B1-0 757 996, all of which are herein fully incorporated by reference.

In one embodiment, bulky ligand metallocene catalysts compounds useful in the invention include bridged heteroatom, mono-bulky ligand metallocene compounds. These types of catalysts and catalyst systems are described in, for example, PCT publication WO 92/00333, WO 94/07928, WO 91/04257, WO 94/03506, WO96/00244, WO 97/15602 and WO 99/20637 and U.S. Patent Nos. 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440 and 5,264,405 and European publication EP-A-0 420 436, all of which are herein fully incorporated by reference.

In this embodiment, the bulky ligand metallocene catalyst compound is represented by the formula:



where M is a Group 3 to 16 metal atom or a metal selected from the Group of actinides and lanthanides of the Periodic Table of Elements, preferably M is a Group 4 to 12 transition metal, and more preferably M is a Group 4, 5 or 6 transition metal, and most preferably M is a Group 4 transition metal in any oxidation state, especially titanium; L^C is a substituted or unsubstituted bulky ligand bonded to M; J is bonded to M; A is bonded to M and J; J is a heteroatom ancillary ligand; and A is a bridging group; Q is a univalent anionic ligand; and n

is the integer 0, 1 or 2. In formula (V) above, L^C , A and J form a fused ring system. In an embodiment, L^C of formula (V) is as defined above for L^A , A, M and Q of formula (V) are as defined above in formula (III).

In formula (V) J is a heteroatom containing ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of Elements. Preferably J contains a nitrogen, phosphorus, oxygen or sulfur atom with nitrogen being most preferred.

In an embodiment of the invention, the bulky ligand metallocene-type catalyst compounds are heterocyclic ligand complexes where the bulky ligands, the ring(s) or ring system(s), include one or more heteroatoms or a combination thereof. Non-limiting examples of heteroatoms include a Group 13 to 16 element, preferably nitrogen, boron, sulfur, oxygen, aluminum, silicon, phosphorous and tin. Examples of these bulky ligand metallocene catalyst compounds are described in WO 96/33202, WO 96/34021, WO 97/17379 and WO 98/22486 and EP-A1-0 874 005 and U.S. Patent No. 5,637,660, 5,539,124, 5,554,775, 5,756,611, 5,233,049, 5,744,417, and 5,856,258 all of which are herein incorporated by reference.

In one embodiment, the bulky ligand metallocene catalyst compounds are those complexes known as transition metal catalysts based on bidentate ligands containing pyridine or quinoline moieties, such as those described in U.S. Application Serial No. 09/103,620 filed June 23, 1998, which is herein incorporated by reference. In another embodiment, the bulky ligand metallocene catalyst compounds are those described in PCT publications WO 99/01481 and WO 98/42664, which are fully incorporated herein by reference.

In another embodiment, the bulky ligand type metallocene catalyst compound is a complex of a metal, preferably a transition metal, a bulky ligand, preferably a substituted or unsubstituted pi-bonded ligand, and one or more heteroallyl moieties, such as those described in U.S. Patent Nos. 5,527,752 and 5,747,406 and EP-B1-0 735 057, all of which are herein fully incorporated by reference.

It is also contemplated that any one of the bulky ligand metallocene catalyst compounds of the invention have at least one fluoride or fluorine containing leaving group as described in U.S. Application Serial No. 09/191,916 filed November 13, 1998.

In another embodiment, the other metal compound or second metal compound is the bulky ligand metallocene catalyst compound is represented by the formula:

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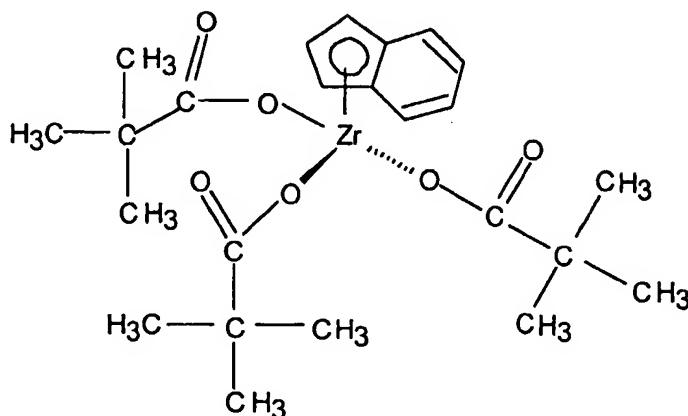


where M is a Group 3 to 16 metal, preferably a Group 4 to 12 transition metal, and most preferably a Group 4, 5 or 6 transition metal; L^D is a bulky ligand that is bonded to M;
 5 each Q is independently bonded to M and $Q_2(YZ)$ forms a ligand, preferably a unicharged polydentate ligand; A or Q is a univalent anionic ligand also bonded to M; X is a univalent anionic group when n is 2 or X is a divalent anionic group when n is 1; n is 1 or 2.

In formula (VI), L and M are as defined above for formula (III). Q is as defined
 10 above for formula (III), preferably Q is selected from the group consisting of -O-, -NR-, -CR₂- and -S-; Y is either C or S; Z is selected from the group consisting of -OR, -NR₂, -CR₃, -SR, -SiR₃, -PR₂, -H, and substituted or unsubstituted aryl groups, with the proviso that when Q is -NR- then Z is selected from one of the group consisting of -OR, -NR₂, -SR, -SiR₃, -PR₂ and -H; R is selected from a group containing carbon, silicon,
 15 nitrogen, oxygen, and/or phosphorus, preferably where R is a hydrocarbon group containing from 1 to 20 carbon atoms, most preferably an alkyl, cycloalkyl, or an aryl group; n is an integer from 1 to 4, preferably 1 or 2; X is a univalent anionic group when n is 2 or X is a divalent anionic group when n is 1; preferably X is a carbamate, carboxylate, or other heteroallyl moiety described by the Q, Y and Z combination.

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In a particularly preferred embodiment the bulky ligand metallocene compound is represented by the formula:



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In a mixed catalyst system, the first and second metal compounds, described above, may be combined at molar ratios of 1:1000 to 1000:1, preferably 1:99 to 99:1, preferably 10:90 to 90:10, more preferably 20:80 to 80:20, more preferably 30:70 to 70:30, more preferably 40:60 to 60:40. The particular ratio chosen will depend on the end product desired and/or the method of activation

Activator and Activation Methods

The metal compounds described herein are typically activated in various ways to yield catalyst compounds having a vacant coordination site that will coordinate, insert and polymerize olefin(s).

For the purposes of this patent specification and appended claims, the term "activator" is defined to be any compound or component or method which can activate any of the Group 15 containing metal compounds and/or the bulky ligand metallocene catalyst compounds of the invention as described above. Non-limiting activators, for example may include a Lewis acid or a non-coordinating ionic activator or ionizing activator or any other compound including Lewis bases, aluminum alkyls, conventional-type cocatalysts and combinations thereof that can convert a neutral bulky ligand metallocene catalyst compound or Group 15

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containing metal compound to a catalytically active Group 15 containing metal compound or bulky ligand metallocene cation. It is within the scope of this invention to use alumoxane or modified alumoxane as an activator, and/or to also use ionizing activators, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) boron, a trisperfluorophenyl boron metalloid precursor or a trisperfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983) or combination thereof, that would ionize the neutral bulky ligand metallocene catalyst and/or the Group 15 containing metal compound.

In one embodiment, an activation method using ionizing ionic compounds not containing an active proton but capable of producing a Group 15 containing metal compound cation or bulky ligand metallocene catalyst cation and their non-coordinating anion are also contemplated, and are described in EP-A- 0 426 637, EP-A- 0 573 403 and U.S. Patent No. 5,387,568, which are all herein incorporated by reference.

There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253, 5,731,451, 5,744,656, 5,847,177, 5,854,166, 5,856,256 and 5,939,346 and European publications EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and EP-B1-0 586 665, and PCT publication WO 94/10180, all of which are herein fully incorporated by reference.

Organoaluminum compounds useful as activators include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like.

Ionizing compounds may contain an active proton, or some other cation associated with but not coordinated to or only loosely coordinated to the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-B1-0 500 944, EP-A-0 277 003 and EP-A-0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299 and 5,502,124 and U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994, all of which are herein fully incorporated by reference.

Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2''- nonafluorobiphenyl) fluoroaluminate, which publication is fully incorporated herein by reference. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP-B1 0 573

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120, PCT publications WO 94/07928 and WO 95/14044 and U.S. Patent Nos. 5,153,157 and 5,453,410 all of which are herein fully incorporated by reference. WO 98/09996 incorporated herein by reference describes activating bulky ligand metallocene catalyst compounds with perchlorates, periodates and iodates including their hydrates. WO 98/30602 and WO 98/30603 incorporated by reference describe the use of lithium (2,2'-bisphenyl-ditrimethylsilicate)•4THF as an activator for a bulky ligand metallocene catalyst compound. WO 99/18135 incorporated herein by reference describes the use of organo-boron-aluminum activators. EP-B1-0 781 299 describes using a silylium salt in combination with a non-coordinating compatible anion. Also, methods of activation such as using radiation (see EP-B1-0 615 981 herein incorporated by reference), electro-chemical oxidation, and the like are also contemplated as activating methods for the purposes of rendering the neutral bulky ligand metallocene catalyst compound or precursor to a bulky ligand metallocene cation capable of polymerizing olefins. Other activators or methods for activating a bulky ligand metallocene catalyst compound are described in for example, U.S. Patent Nos. 5,849,852, 5,859,653 and 5,869,723 and WO 98/32775, WO 99/42467 (dioctadecylmethylammonium-bis(tris(pentafluorophenyl)borane) benzimidazolide), which are herein incorporated by reference.

In one embodiment, the activator is a Lewis acid compound, more preferably an aluminum based Lewis acid compound, and most preferably a neutral, aluminum based Lewis acid compound having at least one, preferably two, halogenated aryl ligands and one or two additional monoanionic ligands not including halogenated aryl ligands. The Lewis acid compounds of this embodiment include those olefin catalyst activator Lewis acids based on aluminum and having at least one bulky, electron-withdrawing ancillary ligand such as the halogenated aryl ligands of tris(perfluorophenyl)borane or tris(perfluoronaphthyl)borane. These bulky ancillary ligands are those sufficient to allow the Lewis acids to function as electronically stabilizing, compatible non-coordinating anions. Stable ionic complexes are achieved when the anions will not be a suitable ligand donor to the strongly Lewis acidic cationic Group 15 containing transition metal cations used in insertion polymerization, i.e., inhibit ligand transfer that would neutralize the cations and render them inactive for polymerization.

The Lewis acids fitting this description of this preferred activator, can be described by the following formula:



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where R is a monoanionic ligand and ArHal is a halogenated C₆ aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together, and n = 1 to 2, preferably n=1.

5 In another embodiment, at least one (ArHal) of formula (VII) is a halogenated C₉ aromatic or higher, preferably a fluorinated naphthyl. Suitable non-limiting R ligands include: substituted or unsubstituted C₁ to C₃₀ hydrocarbyl aliphatic or aromatic groups, substituted meaning that at least one hydrogen on a carbon atom is replaced with a hydrocarbyl, halide, halocarbyl, hydrocarbyl or halocarbyl substituted organometalloid, 10 dialkylamido, alkoxy, siloxy, aryloxy, alkysulfido, arylsulfido, alkylphosphido, alkylphosphido or other anionic substituent; fluoride; bulky alkoxides, where bulky refers to C₄ and higher number hydrocarbyl groups, e.g., up to about C₂₀, such as tert-butoxide and 2,6-dimethyl-phenoxide, and 2,6-di(tert-butyl)phenoxide; -SR; -NR₂, and -PR₂, where each R is independently a substituted or unsubstituted hydrocarbyl as defined above; and, C₁ to C₃₀ 15 hydrocarbyl substituted organometalloid, such as trimethylsilyl.

Examples of ArHal include the phenyl, naphthyl and anthracenyl radicals of U.S. Patent No. 5,198,401 and the biphenyl radicals of WO 97/29845 when halogenated. The use of the terms halogenated or halogenation means for the purposes of this application that at least one third of hydrogen atoms on carbon atoms of the aryl-substituted aromatic ligands 20 are replaced by halogen atoms, and more preferred that the aromatic ligands be perhalogenated. Fluorine is the most preferred halogen.

In another embodiment, the mole ratio of the metal of the activator component to the metal of a supported Group 15 containing catalyst compound are in the range of between 0.3:1 to 1000:1, preferably 20:1 to 800:1, and most preferably 50:1 to 500:1. Where the 25 activator is an ionizing activator such as those based on the anion tetrakis(penta-fluorophenyl)boron, the mole ratio of the metal of the activator component to the metal component of the Group 15 containing hafnium catalyst compound is preferably in the range of between 0.3:1 to 3:1.

It is also within the scope of this invention that the above described Group 15 30 containing metal compounds and/or the bulky ligand metallocene catalyst compounds can

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be combined with one or more of the catalyst compounds represented by formulas (III) through (VI) with one or more activators or activation methods described above.

In another embodiment of the mixed catalyst composition, modified alumoxanes are combined with the first and second metal compounds of the invention to form a catalyst system. In another embodiment MMAO3A (modified methyl alumoxane in heptane, commercially available from Akzo Chemicals, Inc., Holland, under the trade name Modified Methylalumoxane type 3A, see for example those aluminoxanes disclosed in U.S. Patent No. 5,041,584, which is herein incorporated by reference) is combined with the first and second metal compounds to form a catalyst system.

In a particular embodiment, when using the metal compounds represented by Formula 1 and Formula 2, where both are activated with the same activator, the preferred weight percents, based upon the weight of the two metal compounds, but not the activator or any support, are 10 to 95 weight % compound of Formula 1 and 5 to 90 weight % compound of Formula 2, preferably 50 to 90 weight % compound of Formula 1 and 10 to 50 weight % compound of Formula 2, more preferably 60 to 80 weight % compound of formula 1 to 40 to 20 weight % compound of formula 2. In a particularly preferred embodiment the compound of Formula 2 is activated with methylalumoxane, then combined with the compound of Formula 2, then injected in the reactor.

In one particular embodiment, when using Compound I and indenyl zirconium tris-pivalate where both are activated with the same activator, the preferred weight percents, based upon the weight of the two catalysts, but not the activator or any support, are 10 to 95 weight % Compound I and 5 to 90 weight % indenyl zirconium tris-pivalate, preferably 50 to 90 weight % Compound I and 10 to 50 weight % indenyl zirconium tris-pivalate, more preferably 60-80 weight % Compound I to 40 to 20 weight % indenyl zirconium tris-pivalate. In a particularly preferred embodiment the indenyl zirconium tris-pivalate is activated with methylalumoxane, then combined with Compound I, then injected in the reactor.

In general the combined metal compounds and the activator are combined in ratios of about 1000:1 to about 0.5:1. In a preferred embodiment the metal compounds and the activator are combined in a ratio of about 300:1 to about 1:1, preferably about 150:1 to about 1:1, for boranes, borates, aluminates, etc. the ratio is preferably about 1:1 to about 10:1 and

for alkyl aluminum compounds (such as diethylaluminum chloride combined with water) the ratio is preferably about 0.5:1 to about 10:1.

Conventional-Type Catalyst Systems

5 The mixed catalyst composition of the present invention may alternately include the Group 15 containing metal compound, as described above, and a conventional-type transition catalyst.

Conventional-type transition metal catalysts are those traditional Ziegler-Natta, vanadium and Phillips-type catalysts well known in the art. Such as, for example Ziegler-
10 Natta catalysts as described in *Ziegler-Natta Catalysts and Polymerizations*, John Boor, Academic Press, New York, 1979. Examples of conventional-type transition metal catalysts are also discussed in U.S. Patent Nos. 4,115,639, 4,077,904, 4,482,687, 4,564,605, 4,721,763, 4,879,359 and 4,960,741 all of which are herein fully incorporated by reference. The conventional-type transition metal catalyst compounds that may be used in the present
15 invention include transition metal compounds from Groups 3 to 17, preferably 4 to 12, more preferably 4 to 6 of the Periodic Table of Elements.

These conventional-type transition metal catalysts may be represented by the formula: MR_x , where M is a metal from Groups 3 to 17, preferably Group 4 to 6, more preferably Group 4, most preferably titanium; R is a halogen or a hydrocarbyloxy group; and x is the
20 oxidation state of the metal M. Non-limiting examples of R include alkoxy, phenoxy, bromide, chloride and fluoride. Non-limiting examples of conventional-type transition metal catalysts where M is titanium include $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_2H_5)_2Br_2$, $TiCl_3 \cdot 1/3 AlCl_3$ and $Ti(OC_{12}H_{25})Cl_3$.

Conventional-type transition metal catalyst compounds based on magnesium/titanium
25 electron-donor complexes that are useful in the invention are described in, for example, U.S. Patent Nos. 4,302,565 and 4,302,566, which are herein fully incorporate by reference. The $MgTiCl_6$ (ethyl acetate)₄ derivative is particularly preferred.

British Patent Application 2,105,355 and U.S. Patent No. 5,317,036, herein
incorporated by reference, describes various conventional-type vanadium catalyst
30 compounds. Non-limiting examples of conventional-type vanadium catalyst compounds include vanadyl trihalide, alkoxy halides and alkoxides such as $VOCl_3$, $VOCl_2(OBu)$ where

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Bu =butyl and $\text{VO}(\text{OC}_2\text{H}_5)_3$; vanadium tetra-halide and vanadium alkoxy halides such as VCl_4 and $\text{VCl}_3(\text{OBu})$; vanadium and vanadyl acetyl acetonates and chloroacetyl acetonates such as $\text{V}(\text{AcAc})_3$ and $\text{VOCl}_2(\text{AcAc})$ where (AcAc) is an acetyl acetate. The preferred conventional-type vanadium catalyst compounds are VOCl_3 , VCl_4 and $\text{VOCl}_2\text{-OR}$ where R is
 5 a hydrocarbon radical, preferably a C_1 to C_{10} aliphatic or aromatic hydrocarbon radical such as ethyl, phenyl, isopropyl, butyl, propyl, n-butyl, iso-butyl, tertiary-butyl, hexyl, cyclohexyl, naphthyl, etc., and vanadium acetyl acetonates.

Conventional-type chromium catalyst compounds, often referred to as Phillips-type catalysts, suitable for use in the present invention include CrO_3 , chromocene, silyl chromate,
 10 chromyl chloride (CrO_2Cl_2), chromium-2-ethyl-hexanoate, chromium acetylacetonate ($\text{Cr}(\text{AcAc})_3$), and the like. Non-limiting examples are disclosed in U.S. Patent Nos. 3,709,853, 3,709,954, 3,231,550, 3,242,099 and 4,077,904, which are herein fully incorporated by reference.

Still other conventional-type transition metal catalyst compounds and catalyst systems
 15 suitable for use in the present invention are disclosed in U.S. Patent Nos. 4,124,532, 4,302,565, 4,302,566, 4,376,062, 4,379,758, 5,066,737, 5,763,723, 5,849,655, 5,852,144, 5,854,164 and 5,869,585 and published EP-A2 0 416 815 A2 and EP-A1 0 420 436, which are all herein incorporated by reference.

Other catalysts may include cationic catalysts such as AlCl_3 , and other cobalt, iron,
 20 nickel and palladium catalysts well known in the art. See for example U.S. Patent Nos. 3,487,112, 4,472,559, 4,182,814 and 4,689,437 all of which are incorporated herein by reference.

Typically, these conventional-type transition metal catalyst compounds excluding some conventional-type chromium catalyst compounds are activated with one or more of the
 25 conventional-type cocatalysts described below. Also conventional type transition metal catalysts can be activated using the activators described above in this patent specification as appreciated by one in the art.

Conventional-type cocatalyst compounds for the above conventional-type transition metal catalyst compounds may be represented by the formula $\text{M}^3\text{M}^4_\nu\text{X}^2_c\text{R}^3_{b-c}$, wherein M^3 is
 30 a metal from Group 1 to 3 and 12 to 13 of the Periodic Table of Elements; M^4 is a metal of Group 1 of the Periodic Table of Elements; ν is a number from 0 to 1; each X^2 is any halogen; c is a number from 0 to 3; each R^3 is a monovalent hydrocarbon radical or hydrogen; b is a number from 1 to 4; and wherein b minus c is at least 1. Other conventional-type organometallic cocatalyst compounds for the above conventional-type transition metal

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catalysts have the formula $M^3R^3_k$, where M^3 is a Group IA, IIA, IIB or IIIA metal, such as lithium, sodium, beryllium, barium, boron, aluminum, zinc, cadmium, and gallium; k equals 1, 2 or 3 depending upon the valency of M^3 which valency in turn normally depends upon the particular Group to which M^3 belongs; and each R^3 may be any monovalent hydrocarbon radical.

Non-limiting examples of conventional-type organometallic cocatalyst compounds useful with the conventional-type catalyst compounds described above include methyllithium, butyllithium, dihexylmercury, butylmagnesium, diethylcadmium, benzylpotassium, diethylzinc, tri-n-butylaluminum, diisobutyl ethylboron, diethylcadmium, di-n-butylzinc and tri-n-amyloboron, and, in particular, the aluminum alkyls, such as tri-hexylaluminum, triethylaluminum, trimethylaluminum, and tri-isobutylaluminum. Other conventional-type cocatalyst compounds include mono-organohalides and hydrides of Group 2 metals, and mono- or di-organohalides and hydrides of Group 3 and 13 metals. Non-limiting examples of such conventional-type cocatalyst compounds include di-isobutylaluminum bromide, isobutylboron dichloride, methyl magnesium chloride, ethylberyllium chloride, ethylcalcium bromide, di-isobutylaluminum hydride, methylcadmium hydride, diethylboron hydride, hexylberyllium hydride, dipropylboron hydride, octylmagnesium hydride, butylzinc hydride, dichloroboron hydride, di-bromoaluminum hydride and bromocadmium hydride. Conventional-type organometallic cocatalyst compounds are known to those in the art and a more complete discussion of these compounds may be found in U.S. Patent Nos. 3,221,002 and 5,093,415, which are herein fully incorporated by reference.

Supports, Carriers and General Supporting Techniques

The above described Group 15 containing catalysts and/or the mixed catalyst system, including the Group 15 containing catalyst compound and the bulky ligand metallocene catalyst compound, or conventional catalyst compound, may be combined with one or more support materials or carriers using one of the support methods well known in the art or as described below. In one embodiment, the Group 15 containing catalyst or the mixed catalyst system of the invention, is in a supported form, for example deposited on, contacted with, vaporized with, bonded to, or incorporated within, adsorbed or absorbed in, or on, a support or carrier. Also, it is also contemplated that when used in a mixed system, the bulky ligand

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metallocene catalyst supported on a separate carrier than the Group 15 containing catalyst, particularly for use in a reactor system where one supported catalyst system is used in one reactor to produce the high molecular weight component and the other supported catalyst system is used in another reactor to produce the low molecular component.

5 The terms "support" or "carrier" are used interchangeably and are any support material, preferably a porous support material, including inorganic or organic support materials. Non-limiting examples of inorganic support materials include inorganic oxides and inorganic chlorides. Other carriers include resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl
10 benzene polyolefins or polymeric compounds or any other organic or inorganic support material and the like, or mixtures thereof.

 The preferred carriers are inorganic oxides that include those Group 2, 3, 4, 5, 13 or 14 metal oxides. The preferred supports include silica, alumina, silica-alumina, and mixtures thereof. Other useful supports include magnesia, titania, zirconia, magnesium chloride,
15 montmorillonite (EP-B1 0 511 665), phyllosilicate, zeolites, talc, clays and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania and the like. Additional support materials may include those porous acrylic polymers described in EP 0 767 184 B1, which is incorporated herein by reference.

 It is preferred that the carrier, most preferably an inorganic oxide, has a surface area
20 in the range of from about 10 to about 100 m²/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 μm. More preferably, the surface area of the carrier is in the range of from about 50 to about 500 m²/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 μm. Most preferably the surface area of the carrier is in the range is from
25 about 100 to about 400 m²/g, pore volume from about 0.8 to about 5.0 cc/g and average particle size is from about 5 to about 100 μm. The average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000 Å, preferably 50 to about 500 Å, and most preferably 75 to about 450 Å.

 Examples of supporting the catalysts of the invention are described in U.S. Patent
30 Nos. 4,701,432, 4,808,561, 4,912,075, 4,925,821, 4,937,217, 5,008,228, 5,238,892, 5,240,894, 5,332,706, 5,346,925, 5,422,325, 5,466,649, 5,466,766, 5,468,702, 5,529,965, 5,554,704, 5,629,253, 5,639,835, 5,625,015, 5,643,847, 5,665,665, 5,698,487, 5,714,424, 5,723,400, 5,723,402, 5,731,261, 5,759,940, 5,767,032, 5,770,664, 5,846,895 and 5,939,348 and U.S. Application Serial Nos. 271,598 filed July 7, 1994 and 788,736 filed January 23,

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1997 and PCT publications WO 95/32995, WO 95/14044, WO 96/06187 and WO 97/02297, and EP-B1-0 685 494 all of which are herein fully incorporated by reference.

There are various other methods in the art for supporting the polymerization catalyst compound or the mixed catalyst system of the invention. For example, the Group 15
5 containing catalyst compounds and/or the mixed catalyst system including the bulky ligand metallocene catalyst compounds may contain a polymer bound ligand as described in U.S. Patent Nos. 5,473,202 and 5,770,755, which is herein fully incorporated by reference; the Group 15 containing catalyst compounds and/or the bulky ligand metallocene catalyst
10 compounds of the invention may be spray dried as described in U.S. Patent No. 5,648,310, which is herein fully incorporated by reference; the support used with the Group 15 containing metal catalyst compounds and/or the bulky ligand metallocene catalyst compounds of the invention may be functionalized as described in European publication EP-A-0 802 203, which is herein fully incorporated by reference, or at least one substituent or leaving group is selected as described in U.S. Patent No. 5,688,880, which is herein fully
15 incorporated by reference.

In another embodiment, the invention provides for a Group 15 containing catalyst system and/or a mixed system including the bulky ligand metallocene catalyst compounds, which include a surface modifier that is used in the preparation of the supported catalyst system as described in PCT publication WO 96/11960, which is herein fully incorporated by
20 reference. The catalyst systems of the invention can be prepared in the presence of an olefin, for example hexene-1.

In another embodiment, the Group 15 containing hafnium catalyst system and the mixed system including the bulky ligand metallocene catalyst compound can be combined with a carboxylic acid salt of a metal ester, for example aluminum carboxylates such as
25 aluminum mono, di- and tri- stearates, aluminum octoates, oleates and cyclohexylbutyrates, as described in U.S. Application Serial No. 09/113,216, filed July 10, 1998.

A method for producing a supported Group 15 containing catalyst system and/or the bulky ligand metallocene catalyst system is described below and is described in U.S. Application Serial Nos. 265,533, filed June 24, 1994 and 265,532, filed June 24, 1994 and
30 PCT publications WO 96/00245 and WO 96/00243 both published January 4, 1996, all of which are herein fully incorporated by reference. This procedure is used either with the Group 15 containing catalyst compounds together with or separately from the bulky ligand metallocene catalyst compounds. In this method, the catalyst compound or compounds are slurried in a liquid to form a solution and a separate solution is formed containing an activator
35 and a liquid. The liquid may be any compatible solvent or other liquid capable of forming a

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solution or the like with the catalyst compound or compounds and/or activator of the invention. In a preferred embodiment the liquid is a cyclic aliphatic or aromatic hydrocarbon, most preferably toluene. The catalyst compound or compounds and activator solutions are mixed together and added to a porous support such that the total volume of the catalyst
5 compound or compounds solution and the activator solution or the catalyst compound or compounds solution and activator solution is less than four times the pore volume of the porous support, more preferably less than three times, even more preferably less than two times; preferred ranges being from 1.1 times to 3.5 times range and most preferably in the 1.2 to 3 times range.

10 Procedures for measuring the total pore volume of a porous support are well known in the art. Details of one of these procedures is discussed in Volume 1, *Experimental Methods in Catalytic Research* (Academic Press, 1968) (specifically see pages 67-96). This preferred procedure involves the use of a classical BET apparatus for nitrogen absorption. Another method well known in the art is described in Innes, *Total Porosity and Particle Density of*
15 *Fluid Catalysts By Liquid Titration*, Vol. 28, No. 3, Analytical Chemistry 332-334 (March, 1956).

Other methods for supporting the catalyst compounds of the invention are described in U.S. Application Serial Number 09/312,878, filed May 17, 1999, which is fully incorporated herein by reference.

20 When used in a mixed catalyst system, the Group 15 catalyst compound and the bulky ligand metallocene catalyst compound of the invention are combined at molar ratios of 1:1000 to 1000:1, preferably 1:99 to 99:1, preferably 10:90 to 90:10, more preferably 20:80 to 80:20, more preferably 30:70 to 70:30, more preferably 40:60 to 60:40.

In one embodiment of the mixed system of the invention, particularly in a slurry
25 polymerization process, the loading of the total of Group 15 containing compound and the bulky ligand metallocene catalyst compound in μmmol per gram (g) of finished supported catalyst (includes the support material, the mixed catalysts and the activator) is about 40 μmmol per gram, preferably about 38 $\mu\text{mmol/g}$.

In another embodiment, particularly in a gas phase polymerization process utilizing
30 the mixed system of the invention, the loading of the total of Group 15 containing compound and the bulky ligand metallocene catalyst compound in μmmol per gram of finished supported catalyst (includes the support material, the mixed catalysts and the activator) is less than 30 μmmol per gram, preferably less than 25 $\mu\text{mmol/g}$, more preferably less than 20 $\mu\text{mmol/gram}$.

In another embodiment, the R group in formula (VII) above, or ligand, may be covalently bonded to a support material, preferably a metal/metalloid oxide or polymeric support. Lewis base-containing support materials or substrates will react with the Lewis acid activators to form a support bonded Lewis acid compound, a supported activator, where one
5 R group of $R_nAl(ArHal)_{3-n}$ is covalently bonded to the support material. For example, where the support material is silica, the Lewis base hydroxyl groups of the silica is where this method of bonding at one of the aluminum coordination sites occurs. Preferably, in this embodiment, the support material is a metal or metalloid oxide, preferably having surface hydroxyl groups exhibiting a pK_a equal to or less than that observed for amorphous silica,
10 i.e., pK_a less than or equal to about 11.

While not wishing to be bound to any particular theory, it is believed that the covalently bound anionic activator, the Lewis acid, is believed to form initially a dative complex with a silanol group, for example of silica (which acts as a Lewis base), thus forming a formally dipolar (zwitterionic) Bronsted acid structure bound to the
15 metal/metalloid of the metal oxide support. Thereafter, the proton of the Bronsted acid appears to protonate an R-group of the Lewis acid, abstracting it, at which time the Lewis acid becomes covalently bonded to the oxygen atom. The replacement R group of the Lewis acid then becomes $R'-O-$, where R' is a suitable support material or substrate, for example, silica or hydroxyl group-containing polymeric support. Any support material that contain
20 surface hydroxyl groups are suitable for use in this particular supporting method. Other support material include glass beads.

In this embodiment, where the support material is a metal oxide composition, these compositions may additionally contain oxides of other metals, such as those of Al, K, Mg, Na, Si, Ti and Zr and should preferably be treated by thermal and/or chemical means to
25 remove water and free oxygen. Typically such treatment is in a vacuum in a heated oven, in a heated fluidized bed or with dehydrating agents such as organo silanes, siloxanes, alkyl aluminum compounds, etc. The level of treatment should be such that as much retained moisture and oxygen as is possible is removed, but that a chemically significant amount of hydroxyl functionality is retained. Thus calcining at up to 800 °C or more up to a point prior
30 to decomposition of the support material, for several hours is permissible, and if higher loading of supported anionic activator is desired, lower calcining temperatures for lesser times will be suitable. Where the metal oxide is silica, loadings to achieve from less than 0.1 mmol to 3.0 mmol activator/g SiO_2 are typically suitable and can be achieved, for example, by varying the temperature of calcining from 200 to 800+ °C. See Zhuralev, *et al*, Langmuir

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1987, Vol. 3, 316 where correlation between calcining temperature and times and hydroxyl contents of silica's of varying surface areas is described.

The tailoring of hydroxyl groups available as attachment sites can also be accomplished by the pre-treatment, prior to addition of the Lewis acid, with a less than stoichiometric amount of the chemical dehydrating agents. Preferably those used will be used sparingly and will be those having a single ligand reactive with the silanol groups (e.g., $(\text{CH}_3)_3\text{SiCl}$), or otherwise hydrolyzable, so as to minimize interference with the reaction of the transition metal catalyst compounds with the bound activator. If calcining temperatures below 400 °C are employed, difunctional coupling agents (e.g., $(\text{CH}_3)_2\text{SiCl}_2$) may be employed to cap hydrogen bonded pairs of silanol groups which are present under the less severe calcining conditions. See for example, "Investigation of Quantitative SiOH Determination by the Silane Treatment of Disperse Silica", Gorski, *et al*, Journ. of Colloid and Interface Science, Vol. 126, No. 2, Dec. 1988, for discussion of the effect of silane coupling agents for silica polymeric fillers that will also be effective for modification of silanol groups on the catalyst supports of this invention. Similarly, use of the Lewis acid in excess of the stoichiometric amount needed for reaction with the transition metal compounds will serve to neutralize excess silanol groups without significant detrimental effect for catalyst preparation or subsequent polymerization.

Polymeric supports are preferably hydroxyl-functional-group-containing polymeric substrates, but functional groups may be any of the primary alkyl amines, secondary alkyl amines, and others, where the groups are structurally incorporated in a polymeric chain and capable of a acid-base reaction with the Lewis acid such that a ligand filling one coordination site of the aluminum is protonated and replaced by the polymer incorporated functionality. See, for example, the functional group containing polymers of U.S. Patent No. 5,288,677, which is herein incorporated by reference.

Other supports include silica, alumina, silica-alumina, magnesia, titania, zirconia, magnesium chloride, montmorillonite, phyllosilicate, zeolites, talc, clays, silica-chromium, silica-alumina, silica-titania, porous acrylic polymers.

In another embodiment of the invention, olefin(s), preferably C_2 to C_{30} olefin(s) or alpha-olefin(s), preferably ethylene or propylene or combinations thereof are prepolymerized in the presence of a supported Group 15 containing metal catalyst and/or the bulky ligand metallocene catalyst of the invention prior to the main polymerization. The prepolymerization can be carried out batchwise or continuously in gas, solution or slurry phase including at elevated pressures. The prepolymerization can take place with any olefin monomer or combination and/or in the presence of any molecular weight controlling agent

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such as hydrogen. For examples of prepolymerization procedures, see U.S. Patent Nos. 4,748,221, 4,789,359, 4,923,833, 4,921,825, 5,283,278 and 5,705,578 and European publication EP-B-0279 863 and PCT Publication WO 97/44371 all of which are herein fully incorporated by reference.

5

Solution Feed of Group 15 Metal Containing Compound

In another embodiment, the Group 15 containing metal catalyst compound of the invention and the activator are introduced into a slurry or gas phase reactor in a liquid carrier, preferably in a solution. The catalyst and the activator may be fed in separately or together
10 and may be combined immediately before being placed in the reactor or may be contacted for longer periods before being placed in the reactor. Preferred liquid carriers include alkanes, preferably pentane, hexane, isopentane, toluene, cyclohexane, isopentane, heptane, octane, isohexane and the like. Particularly preferred liquid carriers include hexane, pentane, isopentane and toluene.

15 The catalyst system, the metal compounds and/or the activator are preferably introduced into the reactor in one or more solutions. In one embodiment a solution of the activated metal compounds in an alkane such as pentane, hexane, toluene, isopentane or the like is introduced into a gas phase or slurry phase reactor. In another embodiment the catalyst system or the components can be introduced into the reactor in a suspension or an
20 emulsion. In one embodiment, the transition metal compound is contacted with the activator, such as modified methylalumoxane, in a solvent and just before the solution is fed into a gas or slurry phase reactor. In another embodiment a solution of the metal compound is combined with a solution of the activator, allowed to react for a period of time then introduced into the reactor. In a preferred embodiment, the catalyst and activator are allowed
25 to reactor for at least 1 second, preferably at least 5 minutes even more preferably between 5 and 60 minutes, before being introduced into the reactor. The catalyst and activator are typically present at a concentration of 0.0001 to 0.200 mol/l in the solutions, preferably 0.001 to 0.05 mol/l, more preferably 0.005 to 0.025 mol/l. In general the metal compound and the
30 the metal compound and the activator are combined in a ratio of about 300:1 to about 1:1, preferably about 10:1 to about 1:1, for boranes the ratio is preferably about 1:1 to about 10:1

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and for alkyl aluminum compounds (such as diethylaluminum chloride combined with water) the ratio is preferably about 0.5:1 to about 10:1.

In another embodiment, the catalyst system consists of the transition metal compound (catalyst) and/or the activator (cocatalyst) which are preferably introduced into the reactor in solution. Solutions of the metal compounds are prepared by taking the catalyst and
5 dissolving it in any solvent such as an alkane, toluene, xylene, etc. The solvent may first be purified in order to remove any poisons which may affect the catalyst activity, including any trace water and/or oxygenated compounds. Purification of the solvent may be accomplished by using activated alumina and activated supported copper catalyst, for example. The
10 catalyst is preferably completely dissolved into the solution to form a homogeneous solution. Both catalyst and the activator may be dissolved into the same solvent, if desired. Once the catalysts are in solution, they may be stored until use.

For polymerization, it is preferred that the catalyst is combined with an activator prior to injection into the reactor. Additionally, other solvents and reactants can be added to the
15 catalyst solutions (on-line or off-line), to the activator (on-line or off-line), or to the activated catalyst or catalysts.

In a preferred embodiment the catalyst systems of this invention have a productivity of 10,000 grams of polymer per gram of catalyst per hour or more.

The solution fed catalyst system of this invention described above has excellent
20 operability over a wide range of reactor conditions and resin grades from 0.2 dg/min Flow Index to 3 dg/min Melt Index and 0.950 g/cc to 0.916 g/cc density. The catalyst system did not experience any resin agglomeration or sheeting in over 10 days of continuous pilot scale operation. This invention also has the benefit of little or no fouling. No sheets, chunks or rubble were observed during or after the polymerization process. There was no trace of
25 polymer build-up on the inside of the reactor walls or in the recycle gas line. Also, there was no increase in the pressure drop across the heat exchanger, cycle gas compressor or gas distribution plate during the entire run.

Solution Feed of Mixed Catalyst Systems

30 In another embodiment, the mixed catalyst systems of the invention and/or the activator (cocatalyst) are introduced into the reactor in solution. Solutions of the metal

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compounds are prepared by taking the catalyst and dissolving it in any suitable solvent such as an alkane, toluene, xylene, etc. The solvent may first be purified in order to remove any poisons, which may affect the catalyst activity, including any trace water and/or oxygenated compounds. Purification of the solvent may be accomplished by using activated alumina and
5 activated supported copper catalyst. The catalyst is preferably completely dissolved into the solution to form a homogeneous solution. Both catalysts may be dissolved into the same solvent, if desired. Once the catalysts are in solution, they may be stored indefinitely until use.

For polymerization, it preferred that the catalyst is combined with an activator prior to
10 introduction into the reactor. Additionally, other solvents and reactants can be added to the catalyst solutions (on-line or off-line), to the activator (on-line or off-line), or to the activated catalyst or catalysts. See U.S. Patent Nos. 5,317,036 and 5,693,727, EP-A-0 593 083, and WO 97/46599 which are fully incorporated herein by reference, that describe solution feed systems to a reactor. There are many different configurations which are possible to combine
15 the catalysts and activator.

The catalyst systems, the metal compounds and/or the activator(s) may be introduced into the reactor in one or more solutions. The metal compounds may be activated independently, in series or together. In one embodiment, a solution of the two activated metal compounds in an alkane such as pentane, hexane, toluene, isopentane or the like is
20 introduced into a gas phase or slurry phase reactor. In another embodiment the catalysts system or the components can be introduced into the reactor in a suspension or an emulsion. In another embodiment, the second metal compound is contacted with the activator, such as modified methylalumoxane, in a solvent and just before the solution is fed into a gas, slurry or solution phase reactor. A solution of the Group 15 containing metal compound is
25 combined with a solution of the second compound and the activator and then introduced into the reactor.

In the following illustrations, A refers to a catalyst or mixture of catalysts, and B refers to a different catalyst or mixture of catalysts. The mixtures of catalysts in A and B can be the same catalysts, just in different ratios. Further, it is noted that additional solvents or
30 inert gases may be added at many locations.

Illustration 1: A and B plus the activator are mixed off-line and then fed to the reactor.

Illustration 1 is graphically represented in Figure 1.

Illustration 2: A and B are mixed off-line. Activator is added in-line and then fed to the reactor. Illustration 2 is graphically represented in Figure 2.

5 Illustration 3: A or B is contacted with the activator (off-line) and then either A or B is added in-line before entering the reactor. Illustration 3 is graphically represented in Figure 3.

Illustration 4: A or B is contacted with the activator (on-line) and then either A or B is added in-line before entering the reactor. Illustration 4 is graphically represented in Figure 4.

Illustration 5: A and B are each contacted with the activator off-line. Then A and activator
10 and B and activator are contacted in line before entering the reactor. Illustration 5 is graphically represented in Figure 5.

Illustration 6: A and B are each contacted with the activator in-line. Then A and activator
and B and activator are contacted in-line before entering the reactor. (This is a preferred
configuration since the ratio of A to B and the ratio of activator to A and the ratio of activator
15 to B can be controlled independently.). Illustration 6 is graphically represented in Figure 6.

Illustration 7: In this example, A or B is contacted with the activator (on-line) while a
separate solution of either A or B is contacted with activator off-line. Then both stream of A
or B and activator are contacted in-line before entering the reactor. Illustration 7 is
graphically represented in Figure 7.

20 Illustration 8: A is contacted on-line with B. Then, an activator is fed to in-line to the A and B mixture. Illustration 8 is graphically represented in Figure 8.

Illustration 9: A is activated with activator off-line. Then A and activator is contacted on-line with B. Then, an activator is fed to in-line to the A and B and activator mixture.

Illustration 9 is graphically represented in Figure 9.

25

In any of the above illustrations, a means for mixing and/or creating a certain residence time may be employed. For example a mixing blade or screw may be used to mix the components or a certain length pipe may be used to obtain a desired contact or residence time between the components. "On-line" means the material described is in a pipe, tube, or
30 vessel which is directly or indirectly connected to the reactor system. "Off-line" means the material described is in a pipe, tube, or vessel which is not connected to the reactor system.

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In another embodiment this invention relates to a method to polymerize olefins in a gas-phase reactor wherein at least two catalysts and at least one activator are introduced in the polymerization reactor in a liquid carrier. In a preferred embodiment the catalysts and the activator(s) are combined in the liquid carrier before being introduced into the reactor.

5 In another embodiment the catalysts are combined in a liquid carrier then introduced into a channeling means connecting to the reactor and thereafter the activator(s) is introduced into the channeling means at the same or different point as the catalysts. In another embodiment the catalysts are combined in a liquid carrier and thereafter the activator(s) is introduced into the liquid carrier.

10 In another embodiment the liquid carrier containing the catalysts and the activator(s) are placed into an apparatus for introducing the liquid carrier into the reactor. In another embodiment the catalysts and liquid carrier are introduced into the apparatus before the activator is introduced into the apparatus.

In another preferred embodiment the composition comprising the liquid carrier
15 comprises a liquid stream flowing or sprayed into the reactor.

In another preferred embodiment at least one catalyst, at least one activator and the liquid carrier are placed into an apparatus for introduction into the reactor wherein additional catalyst(s) is/are introduced into the apparatus after the first catalyst and activator are introduced into the apparatus.

Polymerization Process

The catalyst composition, catalyst systems, mixed catalyst systems, supported catalyst systems or solution feed catalyst systems of the invention described above are suitable for use in any polymerization process, including solution, gas or slurry processes or a combination
25 thereof. The polymerization process is preferably a gas or slurry phase process and more preferably utilizes a single reactor, and most preferably a single gas phase reactor.

In one embodiment, this invention is directed toward the polymerization or copolymerization reactions involving the polymerization of one or more monomers having from 2 to 30 carbon atoms, preferably 2 to 12 carbon atoms, and more preferably 2 to 8
30 carbon atoms. The invention is particularly well suited to the copolymerization reactions involving the polymerization of one or more olefin monomers of ethylene, propylene, butene-

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1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, 3-methyl-pentene-1, 3,5,5-trimethyl-hexene-1 and cyclic olefins or a combination thereof. Other monomers can include vinyl monomers, diolefins such as dienes, polyenes, norbornene, norbornadiene monomers. Preferably a copolymer of ethylene is produced, where the comonomer is at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, more preferably from 4 to 8 carbon atoms and most preferably from 4 to 7 carbon atoms. In an alternate embodiment, the geminally disubstituted olefins disclosed in WO 98/37109 may be polymerized or copolymerized using the invention herein described.

In another embodiment ethylene or propylene is polymerized with at least two different comonomers to form a terpolymer. The preferred comonomers are a combination of alpha-olefin monomers having 4 to 10 carbon atoms, more preferably 4 to 8 carbon atoms, optionally with at least one diene monomer. The preferred terpolymers include the combinations such as ethylene/butene-1/hexene-1, ethylene/propylene/butene-1, propylene/ethylene/hexene-1, ethylene/propylene/norbornene and the like.

In a particularly preferred embodiment the process of the invention relates to the polymerization of ethylene and at least one comonomer having from 3 to 8 carbon atoms, preferably 4 to 7 carbon atoms. Particularly, the comonomers are butene-1, 4-methyl-pentene-1, hexene-1 and octene-1, the most preferred being hexene-1 and/or butene-1.

Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228 all of which are fully incorporated herein by reference.)

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The reactor pressure in a gas phase process may vary from about 10 psig (69 kPa) to about 500 psig (3448 kPa), preferably in the range of from about 100 psig (690 kPa) to about 400 psig (2759 kPa), preferably in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), more preferably in the range of from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

The reactor temperature in the gas phase process may vary from about 30°C to about 120°C, preferably from about 60°C to about 115°C, more preferably in the range of from about 75°C to 110°C, and most preferably in the range of from about 85°C to about 110°C. Altering the polymerization temperature can also be used as a tool to alter the final polymer product properties.

The productivity of the catalyst or catalyst system is influenced by the main monomer partial pressure. The preferred mole percent of the main monomer, ethylene or propylene, preferably ethylene, is from about 25 to 90 mole percent and the monomer partial pressure is in the range of from about 75 psia (517 kPa) to about 300 psia (2069 kPa), which are typical conditions in a gas phase polymerization process. In one embodiment the ethylene partial pressure is about 220 to 240 psi (1517 to 1653 kPa). In another embodiment the molar ratio of hexene to ethylene in the reactor is 0.03:1 to 0.08:1.

In another embodiment, the reactor utilized in the present invention and the process of the invention produce greater than 500 lbs of polymer per hour (227 Kg/hr) to about 200,000 lbs/hr (90,900 Kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater than 35,000 lbs/hr (15,900 Kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

Other gas phase processes contemplated by the process of the invention include those described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200, EP-A- 0 802 202 and EP-B- 634 421 all of which are herein fully incorporated by reference.

A slurry polymerization process generally uses pressures in the range of from about 1 to about 50 atmospheres and even greater and temperatures in the range of 0°C to about 120°C

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C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

In one embodiment, a preferred polymerization technique of the invention is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Patent No. 3,248,179 which is fully incorporated herein by reference. The preferred temperature in the particle form process is within the range of about 185°F (85°C) to about 230°F (110°C). Two preferred polymerization methods for the slurry process are those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Patent No. 4,613,484, which is herein fully incorporated by reference.

In another embodiment, the slurry process is carried out continuously in a loop reactor. The catalyst as a solution, as a suspension, as an emulsion, as a slurry in isobutane or as a dry free flowing powder is injected regularly to the reactor loop, which is itself filled with circulating slurry of growing polymer particles in a diluent of isobutane containing monomer and comonomer. Hydrogen, optionally, may be added as a molecular weight control. The reactor is maintained at pressure of about 525 psig to 625 psig (3620 kPa to 4309 kPa) and at a temperature in the range of about 140 °F to about 220 °F (about 60 °C to about 104 °C) depending on the desired polymer density. Reaction heat is removed through the loop wall since much of the reactor is in the form of a double-jacketed pipe. The slurry is

allowed to exit the reactor at regular intervals or continuously to a heated low pressure flash vessel, rotary dryer and a nitrogen purge column in sequence for removal of the isobutane diluent and all unreacted monomer and comonomers. The resulting hydrocarbon free powder is then compounded for use in various applications.

5 In an embodiment the reactor used in the slurry process of the invention is capable of producing greater than 2000 lbs of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs/hr (2268 Kg/hr), and most preferably greater than 10,000 lbs/hr (4540 Kg/hr). In another embodiment the slurry reactor used in the process of the invention is producing greater than 15,000 lbs of polymer per hour (6804 Kg/hr), preferably greater than 25,000
10 lbs/hr (11,340 Kg/hr) to about 100,000 lbs/hr (45,500 Kg/hr).

 In another embodiment in the slurry process of the invention the total reactor pressure is in the range of from 400 psig (2758 kPa) to 800 psig (5516 kPa), preferably 450 psig (3103 kPa) to about 700 psig (4827 kPa), more preferably 500 psig (3448 kPa) to about 650 psig (4482 kPa), most preferably from about 525 psig (3620 kPa) to 625 psig (4309 kPa).

15 In another embodiment in the slurry process of the invention the concentration of ethylene in the reactor liquid medium is in the range of from about 1 to 10 weight percent, preferably from about 2 to about 7 weight percent, more preferably from about 2.5 to about 6 weight percent, most preferably from about 3 to about 6 weight percent.

 A preferred process of the invention is where the process, preferably a slurry or gas
20 phase process is operated in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminum, tri-isobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride, dibutyl zinc and the like. This preferred process is described in PCT publication WO 96/08520 and U.S. Patent No. 5,712,352, which are herein fully incorporated by reference.

25 In a preferred embodiment of the invention, a slurry of an aluminum distearate in mineral oil is introduced into the reactor, separately or with the first and/or second metal complex and/or with an activator, from the metal compounds and/or the activators. More information on using aluminum stearate type additives may be found in U.S. Application Serial No. 09/113,261 filed July 10, 1998, which is incorporated by reference herein.

30 In another embodiment, if the second metal compound and Group 15 metal compound of the catalyst system are introduced to the reactor in series, it is preferably that the second

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metal compound is added and/or activated first and that the Group 15 metal compound is added and/or activated second.

In another embodiment, the residence time of the catalyst composition is between about 3 to about 6 hours and preferably between about 3.5 and about 5 hours.

- 5 In an embodiment, the mole ratio of comonomer to ethylene, C_x/C_2 , where C_x is the amount of comonomer and C_2 is the amount of ethylene is between about 0.001 to 0.0100 and more preferably between about 0.002 to 0.008.

The melt index (and other properties) of the polymer produced may be changed by manipulating hydrogen concentration in the polymerization system by:

- 10 1) changing the amount of the first catalyst in the polymerization system, and/or
 2) changing the amount of the second catalyst in the polymerization system, and/or
 3) adding hydrogen to the polymerization process; and/or
 4) changing the amount of liquid and/or gas that is withdrawn and/or purged from the process; and/or
15 5) changing the amount and/or composition of a recovered liquid and/or recovered gas returned to the polymerization process, said recovered liquid or recovered gas being recovered from polymer discharged from the polymerization process; and/or
 6) using a hydrogenation catalyst in the polymerization process; and/or
 7) changing the polymerization temperature; and/or
20 8) changing the ethylene partial pressure in the polymerization process; and/or
 9) changing the ethylene to hexene ratio in the polymerization process; and/or
 10) changing the activator to transition metal ratio in the activation sequence.

- The hydrogen concentration in the reactor is about 100 to 5000 ppm, preferably 200
25 to 2000 ppm, more preferably 250 to 1900 ppm, more preferably 300 to 1800 ppm, and more preferably 350 to 1700 ppm, more preferably 400 to 1600 ppm, more preferably 500 to 1500 ppm, more preferably 500 to 1400 ppm, more preferably 500 to 1200 ppm, more preferably 600 to 1200 ppm, preferably 700 to 1100 ppm, and more preferably 800 to 1000 ppm. The hydrogen concentration in the reactor being inversely proportional to the polymer's weight
30 average molecular weight (M_w).

Polymer of the Invention

The new polymers produced by the process of the present invention may be used in a wide variety of products and end use applications. Preferably the new polymers include polyethylene, and bimodal polyethylene produced in a single reactor by the mixed catalyst system of the invention. In addition to bimodal polymers, it is not beyond the scope of the present application for the mixed system to produce a unimodal or multi-modal polymer.

The Group 15 containing metal compound, when used alone, produces a high weight average molecular weight M_w polymer (such as for example above 100,000, preferably above 150,000, preferably above 200,000, preferably above 250,000, more preferably above 300,000). The second metal compound, when used alone, produces a low molecular weight polymer (such as for example below 80,000, preferably below 70,000, preferably below 60,000, more preferably below 50,000, more preferably below 40,000, more preferably below 30,000, more preferably below 20,000 and above 5,000, more preferably below 20,000 and above 10,000).

The polyolefins, particularly polyethylenes, produced by the present invention, have a density of 0.88 to 0.97g/cm³ (As measured by ASTM 2839). Preferably, polyethylenes having a density of 0.910 to 0.965g/cm³, more preferably 0.915 to 0.960 g/cm³, and even more preferably 0.920 to 0.955 g/cm³ can be produced. In some embodiments, a density of 0.915 to 0.940 g/cm³ would be preferred, in other embodiments densities of 0.930 to 0.970 g/cm³ are preferred.

In a preferred embodiment, the polyolefin recovered typically has a melt index I_2 (as measured by ASTM D-1238, Condition E at 190°C) of about 0.01 to 1000dg/min or less. In a preferred embodiment, the polyolefin is ethylene homopolymer or copolymer. In a preferred embodiment for certain applications, such as films, pipes, molded articles and the like, a melt index of 10dg/min or less is preferred. For some films and molded articles, a melt index of 1dg/min or less is preferred. Polyethylene having a I_2 between 0.01 and 10dg/min is preferred.

In a preferred embodiment the polymer produced herein has an I_{21} (as measured by ASTM-D-1238-F, at 190 °C) of 0.1 to 10dg/min, preferably 0.2 to 7.5dg/min, preferably 2.0dg/min or less, preferably 1.5dg/min or less, preferably 1.2dg/min or less, more preferably between 0.5 and 1.0dg/min, more preferably between 0.6 and 0.8dg/min.

In another embodiment, the polymers of the invention have a melt flow index "MIR" of I_{21}/I_2 of 80 or more, preferably 90 or more, preferably 100 or more, preferably 125 or more.

In another embodiment the polymer has an I_{21} (as measured by ASTM 1238, condition F, at 190 °C)(sometimes referred to as Flow Index) of 2.0dg/min or less, preferably 1.5dg/min or less, preferably 1.2dg/min or less, more preferably between 0.5 and 1.0dg/min, more preferably between 0.6 and 0.8dg/min and an I_{21}/I_2 of 80 or more, preferably 90 or more, preferably 100 or more, preferably 125 or more and has one or more of the following properties in addition:

- (a) M_w/M_n of between 15 and 80, preferably between 20 and 60, preferably between 20 and 40. Molecular weight (M_w and M_n) are measured as described below in the examples section;
- (b) an M_w of 180,000 or more, preferably 200,000 or more, preferably 250,000 or more, preferably 300,000 or more;
- (c) a density (as measured by ASTM 2839) of 0.94 to 0.970 g/cm³; preferably 0.945 to 0.965 g/cm³; preferably 0.950 to 0.960 g/cm³;
- (d) a residual metal content of 5.0 ppm transition metal or less, preferably 2.0 ppm transition metal or less, preferably 1.8 ppm transition metal or less, preferably 1.6 ppm transition metal or less, preferably 1.5 ppm transition metal or less, preferably 2.0 ppm or less of Group 4 metal, preferably 1.8 ppm or less of Group 4 metal, preferably 1.6 ppm or less of Group 4 metal, preferably 1.5 ppm or less of Group 4 metal, preferably 2.0 ppm or less zirconium, preferably 1.8 ppm or less zirconium, preferably 1.6 ppm or less zirconium, preferably 1.5 ppm or less zirconium(as measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICPAES) run against commercially available standards, where the sample is heated so as to fully decompose all organics and the solvent comprises nitric acid and, if any support is present, another acid to dissolve any support (such as hydrofluoric acid to dissolve silica supports) is present;
- (e) 35 weight percent or more high weight average molecular weight component, as measured by size-exclusion chromatography, preferably 40% or more. In a particularly preferred embodiment the higher molecular weight fraction is present at between 35 and 70 weight %, more preferably between 40 and 60 weight %.

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In a preferred embodiment the catalyst composition described above is used to make a polyethylene having a density of between 0.94 and 0.970 g/cm³ (as measured by ASTM D 2839) and an I₂ of 0.5 or less g/10min or less

In another embodiment the catalyst composition described above is used to make a polyethylene having an I₂₁ of less than 10 and a density of between about 0.940 and 0.950g/cm³ or an I₂₁ of less than 20 and a density of about 0.945g/cm³ or less.

In another embodiment, the polymer of the invention is made into a pipe by methods known in the art. For pipe applications, the polymers of the invention have a I₂₁ of from about 2 to about 10 dg/min and preferably from about 2 to about 8dg/min. In another embodiment, the pipe of the invention satisfies ISO qualifications.

In another embodiment, the catalyst composition of the present invention is used to make polyethylene pipe able to withstand at least 50 years at an ambient temperature of 20°C, using water as the internal test medium and either water or air as the outside environment (Hydro static (hoop) stress as measured by ISO TR 9080).

In another embodiment, the polymer has a notch tensile test (resistance to slow crack growth) result of greater than 150hours at 3.0MPa, preferably greater than 500hours at 3.0MPa and more preferably greater than 600 hours at 3.0mPa. (as measured by ASTM-F1473).

In another embodiment, the catalyst composition of the present invention is used to make polyethylene pipe having a predicted S-4 T_c for 110mm pipe of less than -5°C, preferably of less than -15°C and more preferably less than -40°C (ISO DIS 13477/ASTM F1589).

In another embodiment, the polymer has an extrusion rate of greater than about 17lbs/hour/inch of die circumference and preferably greater than about 20lbs/hour/inch of die circumference and more preferably greater than about 22lbs/hour/inch of die circumference

The polyolefins of the invention can be made into films, molded articles (including pipes), sheets, wire and cable coating and the like. The films may be formed by any of the conventional techniques known in the art including extrusion, co-extrusion, lamination, blowing and casting. The film may be obtained by the flat film or tubular process which may be followed by orientation in a uniaxial direction or in two mutually perpendicular directions in the plane of the film to the same or different extents. Orientation may be to the same

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extent in both directions or may be to different extents. Particularly preferred methods to form the polymers into films include extrusion or coextrusion on a blown or cast film line.

In another embodiment, the polymer of the invention is made into a film by methods known in the art. For film application, the polymers of the invention have a I_{21} of from about 2 to about 50dg/min, preferably from about 2 to about 30dg/min, even more preferably from about 2 to about 20dg/min, still more preferably about 5 to about 15 dg/min and yet more preferably from about 5 to about 10dg/min.

In another embodiment, the polymer has an MD Tear of .5mil (13 μ) film of between about 5g/mil and 25g/mil preferably, between about 15g/mil and 25g/mil, and more preferably between about 20g/mil and 25g/mil.

The films produced may further contain additives such as slip, antiblock, antioxidants, pigments, fillers, antifog, UV stabilizers, antistats, polymer processing aids, neutralizers, lubricants, surfactants, pigments, dyes and nucleating agents. Preferred additives include silicon dioxide, synthetic silica, titanium dioxide, polydimethylsiloxane, calcium carbonate, metal stearates, calcium stearate, zinc stearate, talc, BaSO₄, diatomaceous earth, wax, carbon black, flame retarding additives, low molecular weight resins, hydrocarbon resins, glass beads and the like. The additives may be present in the typically effective amounts well known in the art, such as 0.001 weight % to 10 weight %.

In another embodiment, the polymer of the invention is made into a molded article by methods known in the art, for example, by blow molding and injection-stretch molding. For molded applications, the polymers of the invention have a I_{21} of from about 20dg/min to about 50dg/min and preferably from about 35dg/min to about 45dg/min.

In another embodiment, the polymers of the invention, including those described above, have an ash content less than 100ppm, more preferably less than 75ppm, and even more preferably less than 50ppm is produced. In another embodiment, the ash contains negligibly small levels of titanium as measured by Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICPAES) as is well known in the art.

In another embodiment, the polymers of the invention, contain a nitrogen containing ligand detectable by High Resolution Mass Spectroscopy (HRMS) as is well known in the art.

EXAMPLES

In order to provide a better understanding of the present invention, including
5 representative advantages thereof, the following examples are offered.

Definitions:

M_n and M_w were measured by gel permeation chromatography on a waters 150°C GPC
instrument equipped with differential refraction index detectors. The GPC columns were
10 calibrated by running a series of molecular weight standards and the molecular weights were
calculated using Mark Houwink coefficients for the polymer in question.

$$MWD = M_w/M_n$$

Density was measured according to ASTM D 1505.

CDBI (composition distribution breadth index) was measured according to the procedure in
15 WO 93/03093, published February 18, 1993, except that fractions having a molecular weight
below 10,000 M_n were ignored for the calculation.

Melt Index (MI) I_2 was measured according to ASTM D-1238, Condition E, at 190°C.

I_{21} was measured according to ASTM D-1238, Condition F, at 190°C.

Melt Index Ratio (MIR) is the ratio of I_{21} over I_2 as determined by ASTM D-1238.

20 Weight % comonomer was measured by proton NMR.

Dart Impact was measured according to ASTM D 1709.

MD and TD Elmendorf Tear were measured according to ASTM D 1922.

MD and TD 1% Secant modulus were measured according to ASTM D 882.

MD and TD tensile strength and ultimate tensile strength were measured according to ASTM
25 D 882.

MD and TD elongation and ultimate elongation were measured according to ASTM D 412.

MD and TD Modulus were measured according to ASTM 882-91

Haze was measured according to ASTM 1003-95, Condition A.

45° gloss was measured according to ASTM D 2457.

30 BUR is blow up ratio. **26 inch Dart Impact** was measured according to ASTM D 1709,
Method A.

ESCORENE™ LL3002.32 is a linear low density ethylene-hexene copolymer produced in a single gas phase reactor using a Ziegler-Natta catalyst available from Exxon Chemical Company in Houston, Texas, having a density of 0.918 g/cc, an I₂ of 2 dg/min and having a CDBI (composition distribution breadth index) of less than 65.

EXCEED™ ECD 125 is a linear low density ethylene-hexene copolymer produced in a single gas phase reactor using a metallocene catalyst available from Exxon Chemical Company in Houston, Texas, having a density of about 0.91 g/cc, an MI of 1.5 g/10 min.

ESCORENE™ LL3001.63 is a linear low density ethylene-hexene copolymer produced in a single gas phase reactor using a Ziegler-Natta catalyst available from Exxon Chemical Company in Houston, Texas, having a density of 0.918 g/cc, an MI of 1.0 g/10 min.

EXCEED™ 350D60 is a linear low density ethylene-hexene copolymer produced in a single gas phase reactor using a metallocene catalyst available from Exxon Chemical Company in Houston, Texas, having a density of 0.918 g/cc, an MI of 1.0 g/10min and.

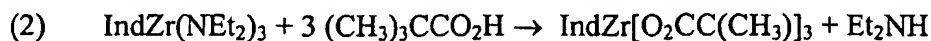
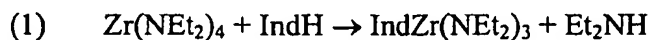
"PPH" is pounds per hour. "mPPH" is millipounds per hour. "ppmw" is parts per million by weight. MD is Machine Direction, TD is Transverse Direction.

The examples in Example Section I, below, utilize of a mixed catalyst system which includes a Group 15 containing metal catalyst and a bulky ligand Metallocene Catalyst.

Example Section I. Mixed Catalyst Systems Including Group 15 Containing Metal Catalyst and Bulky Ligand Metallocene Catalyst

Preparation of Indenyl zirconium tris pivalate

Indenyl zirconium tris pivalate, a bulky ligand metallocene compound, also represented by formula VI, can be prepared by performing the following general reactions:



Where Ind = indenyl and Et is ethyl.

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Preparation of [(2,4,6-Me₃C₆H₂)NHCH₂CH₂]₂NH ligand (Ligand I)

- A 2 L one-armed Schlenk flask was charged with a magnetic stir bar, diethylenetriamine (23.450 g, 0.227 mol), 2-bromomesitylene (90.51 g, 0.455 mol),
- 5 tris(dibenzylideneacetone)dipalladium (1.041 g, 1.14 mmol), racemic-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (racemic BINAP) (2.123 g, 3.41 mmol), sodium tert-butoxide (65.535 g, 0.682 mol), and toluene (800 mL) under dry, oxygen-free nitrogen. The reaction mixture was stirred and heated to 100 °C. After 18 h the reaction was complete, as judged by proton NMR spectroscopy. All remaining manipulations can be performed in air.
- 10 All solvent was removed under vacuum and the residues dissolved in diethyl ether (1 L). The ether was washed with water (3 times with 250 mL) followed by saturated aqueous NaCl (180 g in 500 mL) and dried over magnesium sulfate (30 g). Removal of the ether in vacuo yielded a red oil which was dried at 70 °C for 12 h under vacuum (yield: 71.10 g, 92%). ¹H NMR (C₆D₆) δ 6.83 (s, 4), 3.39 (br s, 2), 2.86 (t, 4), 2.49 (t, 4), 2.27 (s, 12), 2.21 (s, 6), 0.68
- 15 (br s, 1).

Preparation of Catalyst A (for this example section I)**1.5 wt % Catalyst in Toluene Solution**

Note: All procedures below were performed in a glove box.

- 20 1. Weighed out 100 grams of purified toluene into a 1 L Erlenmeyer flask equipped with a Teflon coated stir bar.
2. Added 7.28 grams of Tetrabenzyl Zirconium.
3. Placed solution on agitator and stirred for 5 minutes. All of the solids went into solution.
4. Added 5.42 grams of Ligand I, prepared above.
- 25 5. Added an additional 551 grams of purified toluene and allowed mixture to stir for 15 minutes. No solids remained in the solution.
6. Poured catalyst solution into a clean, purged 1-L Whitey sample cylinder, labeled, removed from glovebox and placed in holding area for operations.

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Alternate Preparation of Compound I $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{Zr}(\text{CH}_2\text{Ph})_2$

A 500 mL round bottom flask was charged with a magnetic stir bar, tetrabenzyl zirconium (Boulder Scientific) (41.729 g, 91.56 mmol), and 300 mL of toluene under dry, oxygen-free nitrogen. Solid ligand I above (32.773 g, 96.52 mmol) was added with stirring over 1 minute (the desired compound precipitates). The volume of the slurry was reduced to 100 mL and 300 mL of pentane added with stirring. The solid yellow-orange product was collected by filtration and dried under vacuum (44.811 g, 80% yield). ^1H NMR (C_6D_6) δ 7.22-6.81 (m, 12), 5.90 (d, 2), 3.38 (m, 2), 3.11 (m, 2), 3.01 (m, 1), 2.49 (m, 4), 2.43 (s, 6), 2.41 (s, 6), 2.18 (s, 6), 1.89 (s, 2), 0.96 (s, 2).

Preparation of Catalyst B (for this example section I)**1 wt% Catalyst B in Hexane Solution)**

All procedures were performed in a glove box.

1. Transfer 1 liter of purified hexane into a 1 L Erlenmeyer flask equipped with a Teflon coated stir bar.
2. Add 6.67 grams of indenyl zirconium tris pivalate dried powder.
3. Place solution on magnetic agitator and stir for 15 minutes. All of the solids go into solution.
4. Pour solution into a clean, purged 1-L Whitey sample cylinder, labeled, and removed from glovebox and place in holding area until use in operation.

Example Section I - Comparative Example 1:

An ethylene-hexene copolymer was produced in a 14-inch (35.6cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18.1 kg/hr), hexene was fed to the reactor at a rate of about 0.6 pounds per hour (0.27 kg/hr) and hydrogen was fed to the reactor at a rate of 5 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 27 PPH. The

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reactor was equipped with a plenum having about 1,900 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor, as described in detail in U.S. Patent No. 5,693,727 which is incorporated herein by reference.) A tapered catalyst injection nozzle having a 0.041 inch (0.10 cm) hole size was positioned in the plenum gas flow. A solution of 1 wt % of Catalyst A in toluene and cocatalyst (MMAO-3A, 1 wt % Aluminum) were mixed in line prior to passing through the injection nozzle into the fluidized bed. (MMAO -3A is modified methyl alumoxane in heptane, commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A .) MMAO to catalyst was controlled so that the Al:Zr molar ratio was 400:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 0.28 dg/min (I_{21}) and 0.935 g/cc (density) properties was obtained. A residual zirconium of 1.63 ppmw was calculated based on a reactor mass balance.

Example Section I - Comparative Example 2:

An ethylene- hexene copolymer was produced in a 14-inch (35.6cm) pilot plant scale gas phase reactor operating at 80° C and 320 psig (2.2 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 37 pounds per hour (19.8 kg/hr), hexene was fed to the reactor at a rate of about 0.4 pounds per hour (0.18 kg/hr) and hydrogen was fed to the reactor at a rate of 12 mPPH. Ethylene was fed to maintain 180 psi (1.2 MPa) ethylene partial pressure in the reactor. The production rate was about 25 PPH. The reactor was equipped with a plenum having about 1,030 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor.) A tapered catalyst injection nozzle having a 0.055 inch (0.14cm) hole size was positioned in the plenum gas flow. A solution of 1 wt % Catalyst B in hexane catalyst was mixed with 0.2 lb/hr (0.09kg/hr) hexene in a 3/16 inch (0.48 cm) stainless steel tube for about 15 minutes. The Catalyst B and hexene mixture were mixed with cocatalyst (MMAO-3A, 1 wt % Aluminum) in a line for about 40 minutes. In addition to the solution, isopentane and nitrogen were added to control particle size. The total system was passed through the injection nozzle into the fluidized bed. MMAO to catalyst ratio was controlled so that the Al:Zr molar ratio was 300:1. A bimodal polymer was produced which was 797 g/10 min

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melt index. The density was 0.9678 g/cc. A residual zirconium of 0.7 ppmw was calculated based on a reactor mass balance. SEC analysis and deconvolution using 4 floury distributions was completed and the results are shown in Table I.

5 **Example Section I - Example 3:**

 An ethylene-hexene copolymer was produced in a 14-inch (35.6cm) pilot plant scale gas phase reactor operating at 80° C and 320 psig (2.2 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 53 pounds per hour (24 kg/hr), hexene was fed to the reactor at a rate of about 0.5 pounds per hour (0.22 kg/hr) and hydrogen was fed to the reactor at a rate of 9 mPPH. Ethylene was fed to maintain 220 psi (1.52 MPa) ethylene partial pressure in the reactor. The production rate was about 25 PPH. The reactor was equipped with a plenum having about 990 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor.) A tapered catalyst injection nozzle having a 0.055 inch (0.12) hole size was positioned in the plenum gas flow. A solution of 1 wt % Catalyst B in hexane catalyst was mixed with 0.2 lb/hr (0.09 kg/hr) hexene in a 3/16 inch (0.48 cm) stainless steel tube for about 15 minutes. The Catalyst B and hexene mixture were mixed with cocatalyst (MMAO-3A, 1 wt % Aluminum) in a line for about 20-25 minutes. In a separate activating stainless steel tube, a 1wt % Catalyst A in toluene solution was activated with cocatalyst (MMAO-3A, 1 wt % Aluminum) for about 50-55 minutes. The two independently activated solutions were combined into a single process line for about 4 minutes. The quantity of Catalyst A catalyst was about 40-45 mol% of the total solution fed. In addition to the solution, isopentane and nitrogen were added to control particle size. The total system was passed through the injection nozzle into the fluidized bed. MMAO to catalyst ratio was controlled so that the Al:Zr molar ratio was 300:1. A bimodal polymer was produced which was 0.045 g/10min melt index and 7.48 g/10min flow index. The density was 0.9496 g/cc. A residual zirconium of 1.7 ppmw was calculated based on a reactor mass balance. SEC analysis and deconvolution using 7-8 floury distributions was completed and the results are shown in Table I.

Example Section I - Example 4:

An ethylene-hexene copolymer was produced in a 14-inch (35.6cm) pilot plant scale gas phase reactor operating at 85° C and 320 psig (2.2 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 50 pounds per hour (22.7 kg/hr), some of the hexene was fed to the reactor at a rate of about 0.7 pounds per hour (0.32 kg/hr) and hydrogen was fed to the reactor at a rate of 11 mPPH. Ethylene was fed to maintain 220 psi (1.52 MPa) ethylene partial pressure in the reactor. The production rate was about 29 PPH. The reactor was equipped with a plenum having about 970 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor.) A tapered catalyst injection nozzle having a 0.055 inch (0.14cm) hole size was positioned in the plenum gas flow. A solution of 1 wt % Catalyst B in hexane catalyst was mixed with 0.2 lb/hr (0.09 kg/hr) hexene in a 3/16 inch (0.48 cm) stainless steel tube for about 15 minutes. The Catalyst B and hexene mixture were mixed with cocatalyst (MMAO-3A, 1 wt % Aluminum) in a line for about 20-25 minutes. In a separate activating stainless steel tube, a 1wt % Catalyst A in toluene solution was activated with cocatalyst (MMAO-3A, 1 wt % Aluminum) for about 50-55 minutes. The two independently activated solutions were combined into a single process line for about 4 minutes. The quantity of Catalyst A catalyst was about 40-45 mol% of the total solution fed. In addition to the solution, isopentane and nitrogen were added to control particle size. The total system was passed through the injection nozzle into the fluidized bed. MMAO to catalyst was controlled so that the Al:Zr molar ratio was 300:1. A bimodal polymer was produced which was 0.054 g/10min melt index and 7.94 g/10min flow index. The density was 0.948 g/cc. A residual zirconium of 1.1 ppmw was calculated based on a reactor mass balance. SEC analysis and deconvolution using 7-8 floury distributions was completed and the results are shown in Table I.

Example Section I - Example 5:

An ethylene-hexene copolymer was produced in a 14-inch (35.6cm) pilot plant scale gas phase reactor operating at 85° C and 320 psig (2.2 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 60 pounds per

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hour (27.2 kg/hr), hexene was fed to the reactor at a rate of about 0.8 pounds per hour (0.36 kg/hr) and hydrogen was fed to the reactor at a rate of 13 mPPH. Ethylene was fed to maintain 220 psi (1.52 MPa) ethylene partial pressure in the reactor. The production rate was about 34 PPH. The reactor was equipped with a plenum having about 960 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor.) A tapered catalyst injection nozzle having a 0.055 inch (0.14cm) was positioned in the plenum gas flow. A solution of 1 wt % Catalyst B in hexane catalyst was mixed with 0.2 lb/hr (0.09 kg/hr) hexene in a 3/16 inch (0.48 cm) stainless steel tube for about 15 minutes. The Catalyst B and hexene mixture were mixed with cocatalyst (MMAO-3A, 1 wt % Aluminum) in a line for about 20-25 minutes. In a separate activating stainless steel tube, a 1wt % Catalyst A in toluene solution was activated with cocatalyst (MMAO-3A, 1 wt % Aluminum) for about 50-55 minutes. The two independently activated solutions were combined into a single process line for about 4 minutes. The quantity of Catalyst A catalyst was about 40-45 mol% of the total solution fed. In addition to the solution, isopentane and nitrogen were added to control particle size. The total system was passed through the injection nozzle into the fluidized bed. MMAO to catalyst ratio was controlled so that the Al:Zr molar ratio was 300:1. A bimodal polymer was produced which was 0.077 g/10min melt index and 12.7 g/10min flow index. The density was 0.9487 g/cc. A residual zirconium of 0.9 ppmw was calculated based on a reactor mass balance. SEC analysis and deconvolution using 7-8 floury distributions was completed and the results are shown in Table I.

Example Section I - Example 6:

An ethylene-hexene copolymer was produced in a 14-inch (35.6cm) pilot plant scale gas phase reactor operating at 85° C and 320 psig (2.2 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 60 pounds per hour (27.2 kg/hr), hexene was fed to the reactor at a rate of about 0.8 pounds per hour (0.36 kg/hr) and hydrogen was fed to the reactor at a rate of 13 mPPH. Ethylene was fed to maintain 220 psi (1.52 MPa) ethylene partial pressure in the reactor. The production rate was about 34 PPH. The reactor was equipped with a plenum having about 1,100 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-

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phase reactor.) A tapered catalyst injection nozzle having a 0.055 inch (0.14cm) was positioned in the plenum gas flow. A solution of 1 wt % Catalyst B in hexane catalyst was mixed with 0.2 lb/hr (0.09 kg/hr) hexene in a 3/16 inch (0.48 cm) stainless steel tube for about 15 minutes. The Catalyst B and hexene mixture were mixed with cocatalyst (MMAO-3A, 1 wt % Aluminum) in a line for about 10-15 minutes. 1wt % Catalyst A in toluene solution was added to the activated Catalyst B solution for about 5 minutes before being sprayed into the reactor. The quantity of Catalyst A catalyst was about 40-45 mol% of the total solution fed. In addition to the solution, isopentane and nitrogen were added to control particle size. The total system was passed through the injection nozzle into the fluidized bed. MMAO to catalyst ratio was controlled so that the final Al:Zr molar ratio was 300:1. A bimodal polymer was produced which was 0.136 g/10min melt index and 38.1 g/10min flow index. The density was 0.9488g/cc. A residual zirconium of 0.5 ppmw was calculated based on a reactor mass balance. SEC analysis and deconvolution using 7-8 floury distributions was completed and the results are shown in Table I.

Example Section I - Example 7:

An ethylene-hexene copolymer was produced in a 14-inch (35.6cm)pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 42 pounds per hour (19.1 kg/hr), hexene was fed to the reactor at a rate of about 0.8 pounds per hour (0.36 kg/hr) and hydrogen was fed to the reactor at a rate of 13 mPPH. Ethylene was fed to maintain 220 psi (1.52 MPa) ethylene partial pressure in the reactor. The production rate was about 32 PPH. The reactor was equipped with a plenum having about 2010 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor.) A tapered catalyst injection nozzle having a 0.055 inch (0.14cm) was positioned in the plenum gas flow. A solution of 0.25 wt % Catalyst B in hexane catalyst was mixed with 0.1 lb/hr (0.05 kg/hr) hexene in a 3/16 inch (0.48 cm) stainless steel tube. The Catalyst B and hexene mixture were mixed with cocatalyst (MMAO-3A, 1 wt % Aluminum) in a line for about 15 minutes. 0.5wt % Catalyst A in toluene solution was added to the activated Catalyst B solution for about 15 minutes before being sprayed into the reactor. The quantity of Catalyst A catalyst was about 65-70 mol% of the total solution fed. In addition to

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the solution, isopentane and nitrogen were added to control particle size. The total system was passed through the injection nozzle into the fluidized bed. MMAO to catalyst ratio was controlled so that the final Al:Zr molar ratio was 500. A bimodal polymer was produced which was 0.06 g/10min melt index and 6.26 g/10min flow index. The density was 0.9501 g/cc. A residual zirconium of 0.65 ppmw was calculated based on a reactor mass balance. SEC analysis and deconvolution using 7-8 floury distributions was completed and the results are shown in Table I.

Table I

Example	1 (Comp)	2(Comp)	3	4	5	6	7
I ₂₁ (dg/min)	0.28	n/a	7.5	7.94	12.6	38.1	6.26
I ₂₁ /I ₂	---	---	165.3	147	164.6	280.4	104
I ₂ (dg/min)	no flow	797	0.045	0.054	0.077	0.136	0.060
Experimental SEC Data							
Mn	80,600	2,952	7,908	10,896	10,778	10,282	8,700
Mw	407,375	13,398	340,011	263,839	259,389	261,138	287,961
Mw/Mn	5.05	4.54	43	24.2	24.1	25.4	33.10
Mn (calculated)	---	---	7,645	10,552	10,673	10,105	8,523
Mw (calculated)	---	---	339,752	258,282	248,215	252,310	284,814
Mw/Mn (calculated)	---	---	44.44	24.48	23.26	24.97	33.42
LMW Mn (calculated)	---	2,988	3,741	5,548	5,731	6,382	4,165
LMW Mw (calc.)	---	13,214	13,259	16,388	15,214	18,333	11,771
LMW Mw/Mn (calc.)	---	4.42	3.54	2.95	2.65	2.87	2.83
HMW Mn (calculated)	73,979	---	122,758	111,256	85,461	88,374	115,954
HMW Mw (calc.)	407,513	---	633,154	501,013	484,657	607,625	526,630
HMW Mw/Mn (calc.)	5.51	---	5.16	4.50	5.67	6.88	4.54
SPLIT (HMW/Total)	100.00	0.00	52.67	49.92	49.64	39.70	53.03
Reactor Conditions							
Reactor Temp (°C)	85	80	80	85	85	85	85
C ₂ psi /Mpa	220/1.52	180/1.24	220/1.52	220/1.52	220/1.52	220/1.52	220/1.52
H ₂ /C ₂ mole ratio	0.0016	0.0018	0.0013	0.0014	0.0014	0.0010	0.0019
C ₆ /C ₂ mole ratio	0.00488	0.00153	0.0074	0.0073	0.0077	0.0075	0.0050
Residence time (hr)	3.6	7.5	5.3	4.74	3.87	3.87	3.4
Molar ratio HMW/LMW	---	---	0.71	0.73	0.76	0.76	2.16
Molar %Catalyst A	100	---	41	42	43	43	68
Zr ppm, by lab	---	---	1.33	1.61	1.33	0.8	0.97
Zr ppm, by feed	1.63	---	1.46	1.06	0.9	0.54	0.62
Average	1.63	---	1.40	1.34	1.12	0.67	0.80
Al/Zr mole ratio	400	---	330	380	320	307	500
Catalyst B activity g PE/mmol cat-hr	---	---	9,965	12,515	18,754	37,288	50,142
Catalyst A activity g PE/mmol cat-hr	15,559	---	15,730	17,042	24,323	32,465	26,203

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Section I - Comparative Examples 1 and 2 give experimental data on how the single component catalyst system behave. Examples 3 and 4 demonstrate the effect of temperature on essentially the same reactor conditions and catalyst feed system. Note that at higher temperature, the M_w/M_n is lower, as is the MFR. Examples 5 and 6 compare the effect of
5 activation scheme for essentially the same reactor conditions and catalyst feed system. Note that in Example 6, the overall activity of the catalyst is better. However, the amount of high molecular weight material produced is lower. Examples 6 and 7 demonstrate the ability to control the amount of high molecular weight material produced at essentially similar reactor conditions. Example 7 fed a higher percentage of Catalyst A feed, hence a higher quantity of
10 higher Mw material was produced.

Example Section I - Example 8:

350 pounds (159 kg) of polyethylene produced according to example 4 above (referred to as Polymer A) was compounded on a Werner-Fleiderer ZSK-30 twin screw extruder with 1000 ppm Irganox™ 1076 and 1500 ppm Irgafos™ 1068 at a melt temperature
15 of 220°C and formed into pellets. Then the pellets were blown into a 0.5 mil (13 µm) film on an Alpine blown film extrusion line. The extrusion condition were: die-160 mm triplex, 1.5 mm die gap, 400 ° C die temperature, 48 inches (122 cm) layflat width, target melt temperature- 410°F (210 °C), and extrusion rates- 310 lb/hr (144 kg/hr), 420 lb/hr (191 kg/hr) and 460 lb/hr (209 kg/hr). ESCORENE™ HD7755.10 (a conventional series reactor product
20 of Exxon Chemical Company, Houston, Texas) was run at the same conditions as a comparison. All films were conditioned according to 23°C, 50% humidity for 40 hours. The data are reported in Table IA.

Table IA

	Polymer A	HD7755.10	Polymer A	HD7755.10	Polymer A	HD7755.10
Rate lb/hr/ (kg/hr)	317 (144)	317 (144)	421 (191)	421 (191)	460 (209)	460 (209)
Film Gage	0.524 mil / 13 μ m	0.502 mil / 13 μ m	0.532 mil / 14 μ m	0.519 mil / 13 μ m	0.543 mil / 14 μ m	0.528 mil / 13 μ m
Density g/cc	0.9489	0.949	0.9502	0.949	0.9468	0.9489
26" (66cm) dart @ 1day	355 g	308 g	327 g	325 g	Nm	nm
26" (66 cm) dart @7days	351 g	308 g	314 g	344 g	301 g	360 g
MD Tear g/mil (g/ μ)	22 (0.87)	16(0.63)	25(0.98)	15(0.59)	22(0.87)	15(0.59)
TD Tear g/mil (g/ μ)	97(3.82)	102(4.02)	77(3.03)	84(3.31)	100(3.94)	81(3.19)
1% Secant MD,psi(MPa)	161,000 (1110)	200,200 (1380)	159,000 (1096)	183,800 (1267)	156,200 (1077)	178,700 (1232)
1% Secant TD,psi (MPa)	184,500 (1272)	212,500 (1465)	163,500 (1127)	206,600 (1425)	161,400 (1113)	212,500 (1465)
MD UT Str. Psi (MPa)	14445 (100)	14347 (99)	12574 (87)	15110 (104)	12934 (89)	15609 (108)
TD UT Str. Psi (MPa)	13369 (92)	12124 (84)	10785 (74)	12278 (85)	11727 (81)	11482 (79)
U Elong. %	285	293	246	296	253	299
U. Elon. %	317	393	305	377	340	377
Haze %	59.6	64.0	57.8	62.0	56.9	60.9
45° Gloss	13.6	10.8	13.4	12.0	14.9	11.9

MD = Machine Direction, TD = Transverse Direction, UT Str = Ultimate Tensile strength

U. Elong = Ultimate Elongation

- 5 ESCORENE HD7755.10 is a polyethylene polymer available from Exxon Chemical Company, Houston, Texas, having an I_{21} of 7.5, and MIR of 125, an M_w of 180,000, a density of 0.95 g/cc, produced using a dual reactor system.

Example Section I - Example 9:

Several drums of granular samples (produced following the polymerization procedure above with a molar catalyst ratio (Catalyst A / Catalyst B) of 2.3 were tumble mixed with 1000 ppm Irganox™ 1076 and 1500 ppm Irgafos™ 1068 and 1500 ppm of calcium stearate.

- 5 This tumble-mixed granular resin was pelletized on a 2 ½" (6.35 cm) Prodex compounding line at 400°F (204° C). Thus prepared pellets were film extruded on a 50mm Alpine blown film line which is equipped with an extruder with 50mm single screw (18:1 L/D ratio) and 100mm annular die with 1 mm die gap. The extrusion conditions were: 400 ° F (204° C) die temperature, output rate- 100 lb/hr (46kg/hr). A typical set temperature profile was:
- 10 380°F/400°F/400°F/400°F/400°F/400°F/410°F/410°F (193°C/204°C/204°C/204°C/204°C/204°C/210°C/210°C) for Barrel1/ Barrel2/Block adaptor/Bottom adaptor/Verical adaptor/Die bottom/Die middle/Die top. The pellet samples were extruded to produce 1.0 mil (25µm) film sample at the line speed of 92 fpm (48 cm/sec) and 0.5 mil (13 µm) film sample at the line speed of 184 fpm (94 cm/sec) at the blow-up ratio (BUR) of 4.0. For both cases the
- 15 bubble showed excellent stability with a typical "necked-in" wine glass shape. The FLH (frost line height) of blown bubble was maintained at 36 inches (91.4cm) and 40 inches (101.6cm), respectively for 1.0 mil (25 µm) and 0.5 mil (12.5 µm) film. The extrusion head pressure and motor load exhibited slightly higher than ESCORENE™ HD7755.10 (a conventional series reactor product of Exxon Chemical Company in Mt Belvue Texas) at the
- 20 same extrusion conditions. The resultant film properties are reported in Table IB. All the film samples were conditioned at to 23°C, 50% humidity for 40 hours. Dart impact strength of 0.5 mil (12.5 µm) film exhibited 380g, which exceeded that of ESCORENE™ HD7755.10 which showed 330g.

Table IB

	Escorene™ 7755		Polymer B	
I ₂ (g/10min)	0.08		0.062	
I ₂₁ (g/10min)	10		10.02	
I ₂₁ /I ₂	134		160.5	
Density (g/cc)	0.952		0.9485	
Output (lb/hr) (kg/hr)	104 (47)		100 (47)	
Die rate (lb/hr/in die)	~8		~8	
Head pressure psi/MPa	7,200(50)		7600(53)	
Motor Load (amp)	56		61	
BUR	4		4	
FLH (inch)(cm)	36(91.4)	40(101.6)	36(91.4)	40(101.6)
Melt fracture	no		No	no
Bubble Stability	good		Good	good
Take-up (fpm)(m/s)	92(0.5)	185(0.9)	92(0.5)	184 (0.9)
Film gauge (mil)(μ)	1(25)	0.5(12.5)	1 (25)	0.5(12.5)
Dart Impact strength (g)	250	330	290	360
Tensile str. (psi)(MPa)				
MD	8,400(58)	11,300(78)	8100(56)	11400(79)
TD	7,900(55)	10,400(72)	7230(50)	9520(66)
Elongation (%)				
MD	350	230	410	330
TD	570	390	580	410
Elmendorf Tear (g/mil)(g/μ)				
MD	25(0.98)	22(0.87)	24(0.95)	33(1.30)
TD	142(5.59)	72(2.83)	205(8.07)	71(2.80)
Modulus (psi)(MPa)				
MD	127,000(876)	144,000(993)	131500(907)	135350(933)
TD	146,000(1007)	169,000(1165)	160250(1105)	156300(1078)

MD = machine direction, TD= transverse direction.

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Example Section I - Example 10:

Following the procedure of Example 9, several drums of granular samples (Polymer C produced following the polymerization procedure above with a molar catalyst ratio of Catalyst A to Catalyst B of 0.732 and Polymer D produced following the polymerization procedure above with a molar catalyst ratio of Catalyst A to Catalyst B of 2.6) were tumble
5 mixed with 1000 ppm Irganox™ 1076, 1500 ppm of calcium stearate and 1500 ppm Irgafos™ 1068 then pelletized and extruded as described in Example 9. All films were conditioned at 23°C and 50% humidity for 40 hours. Dart impact strength of a 0.5 mil (12.5 um) film from both Polymer C and Polymer D exhibited 380g, which exceeded that of ESCORENE™ HD
10 7755.10 which showed 330g. The data are reported in Table IC.

Table IC

Sample	Polymer C		Polymer D		Escorene 7755	
Rxn Temp (oC)	85		85			
C ₂ (psi)(kPa)	220 (1517)		220 (1517)			
H ₂ /C ₂ (molar)	0.0014-0.0016		0.00102			
C ₆ /C ₂ (molar)	0.0075-0.0078		0.00531-0.00586			
Mn	14,600		16,400			
Mw	309,100		298,200		291,500	
Mw/Mn	21.2		18.2		15.7	
HMW/LMW	53.8 /46.2		50.5 /49.5			
I ₂ (g/10min)	0.056		0.049		0.08	
I ₂₁ (g/10min)	6.48		6.7		10	
MFR (I ₂₁ /I ₂)	115.8		138		134	
Density (g/cc)	0.9487		0.9461		0.952	
Output (lb/hr)(kg/hr)	102 (46)		102 (46)		100 (45)	
Die rate (lb/hr/in die)	~8		~8		10	
Head.(psi)(MPa)	8,120 (56)		7,890 (54)		7,230 (50)	
Motor Load (amp)	64.5		63		59	
BUR	4		4		4	
FLH (inch)(cm)	40(101.6)	40(101.6)	36(91.4)	40(101.6)	36(91.4)	40(101.6)
melt fracture	no		No		no	
Bubble Stability	Fair	Good	Good	Good	Good	Good
Filmgauge (mil)(μm)	1(25.4)	0.5(12.7)	1(25.4)	0.5(12.7)	1(25.4)	0.5(12.7)
Dart Impact (g)	200	380	200	380	250	330
Tensile strength						
MD (psi)(MPa)	10,300 (71)	19,900 (137)	9,900 (68)	15,500 (107)	8,400 (58)	11,300 (78)
TD (psi)(MPa)	7,900 (55)	13,800 (95)	8,400 (58)	14,500 (100)	7,900 (55)	10,400 (72)
Elongation (%)						
MD	320	240	290	250	350	230
TD	630	385	610	350	570	390
Elmendorf Tear						
MD (g/mil)(g/μm)	24(0.95)	21(0.83)	36(1.42)	36(1.42)	25(0.98)	22(0.87)
TD (g/mil)(g/μm)	410(16.1)	87(3.4)	350(13.8)	66(2.6)	142(5.6)	72(2.8)
Modulus						
MD (kpsi)(MPa)	105(724)	120(827)	103(710)	110(758)	127(876)	144(993)
TD (psi)(MPa)	128(883)	126(869)	129(889)	114(786)	146(1007)	169(1165)

Alpine line, 2" screw, 4 inch (10.2 cm) die, 40 mil(1016μm) die gap,
410°F (210°C) die set Temp.

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In addition to the examples above, other variations on polymerizing using the catalyst systems described herein include:

1. Compound I could be dissolved in a solvent, preferably toluene to form the desired weight % solution then used in combination with other catalyst systems.
2. Catalyst A could be used as a 0.50 weight % solution in toluene and Catalyst B could be used as a 0.25 weight % solution in hexane at molar ratios of B to A of about 0.7 when the two are activated separately then mixed together (parallel activation) or at molar ratios of B to A of 2.2 to 1.5 when A is activated then B is added (sequential activation).
3. Raising or lowering the reaction temperature to narrow or broaden the Mw/Mn, respectively.
4. Changing residence time to affect product properties. Large changes can have significant impact. One to five, preferably four hours residence time appears to produce good product properties.
5. Spraying the catalyst into the reactor in such a way as to create a particle lean zone. A particle lean zone can be created by a 50,000 lb/hr flow of cycle gas through 6 inch pipe. The catalyst can be atomized w/ a spray nozzle using nitrogen atomizing gas.
6. The activator, preferably MMAO 3A can be used at 7 weight % al in isopentane , hexane or heptane at feed rate sufficient to give an Al/Zr ratio of 100 to 300.
7. Catalyst A is mixed on-line with MMAO 3A then Catalyst B is added on line, then the mixture is introduced into the reactor.
7. Catalyst A is mixed on-line with MMAO 3A and Catalyst B is mixed on line with MMAO 3A thereafter the two activated catalysts are mixed on-line then introduced into the reactor.

The examples in Example Section II, below, utilize a catalyst system which includes a Group 15 containing metal catalyst having benzyl leaving groups.

5

Example Section II. Catalyst Systems Including Group 15 Containing Metal Catalyst with Benzyl Leaving Groups

The $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NHCH}_2\text{CH}_2]_2$ or (NH ligand), and the $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{Zr}(\text{CH}_2\text{Ph})_2$ or (Zr-HN3) were prepared as above in example section I.

Preparation of $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{ZrCl}_2$ or (ZrCl₂-HN3)

5.480 g of $\text{Zr}(\text{NMe}_2)_4$ (20.48 mmol) was dissolved in 50 mL of pentane in a 250 mL round bottom flask. 6.656 g of $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NHCH}_2\text{CH}_2]_2\text{NH}$ (20.48 mmol) was added as a pentane solution (50 mL) and the solution stirred for 2 hours. The mixed amide $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{Zr}(\text{NMe}_2)_2$ was identified by proton NMR but was not isolated. ^1H NMR (C_6D_6) δ 6.94 (m, 4), 3.33 (m, 2), 3.05 (s, 6), 3.00 (m, 2), 2.59 (m, 4), 2.45 (s, 6), 2.43 (s, 6), 2.27 (s, 6), 2.20 (s, 6), 1.80 (m, 1). The solvent was removed under vacuum. The residues were dissolved in toluene and 6.0 g of ClSiMe_3 (55 mmol) added in one portion. The solution was stirred for 24 hours. The solvent was removed under vacuum and the solids suspended in pentane. The solid was collected by filtration and wash with pentane (5.528 g, 54% yield). The dichloride $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{ZrCl}_2$ was identified by proton NMR. ^1H NMR (C_6D_6) δ 6.88 (s, 2), 6.81 (s, 2), 3.32 (m, 2), 2.86 (m, 2), 2.49 (s, 6), 2.47 (m, 4), 2.39 (s, 6), 2.12 (s, 6), NH was obscured.

Preparation of Catalyst A (for purposes of this example section II)

To 2.051 g of MAO (6.836 g of a 30 weight percent solution in toluene, available from Albemarle Corporation, Baton Rouge, Louisiana) and 7.285 g of toluene in a 100 mL round bottom flask was added 0.145 g of $\text{ZrCl}_2\text{-HN3}$. The solution was stirred for 15 minutes. 5.070 g of silica (Davison 948, calcined at 600°C available from W.R. Grace, Davison Division, Baltimore, Maryland) was added followed by mixing. The mixture was dried overnight under vacuum affording 7.011 g of finished catalyst with a loading of 0.36 weight percent zirconium and an Al/Zr ratio of 122:1.

Preparation of Catalyst B (for purposes of this example section II)

To 0.801 g of MAO (2.670 g of a 30 weight percent solution in toluene, available from Albemarle Corporation, Baton Rouge, Louisiana) and 4.679 g of toluene in a 100 mL round bottom flask was added 0.070 g of Zr-HN3. The solution was stirred for 15 minutes. 2.130 g of silica (Davison 948, calcined at 600°C, available from W.R. Grace, Davison Division, Baltimore, Maryland) was added followed by mixing. The mixture was dried overnight under vacuum affording 2.899 g of finished catalyst with a loading of 0.35 weight percent zirconium and an Al/Zr ratio of 120:1.

Example Section II - Comparative Example 1 Slurry-Phase Ethylene Polymerization with Catalyst A

Polymerization was performed in the slurry-phase in a 1-liter autoclave reactor equipped with a mechanical stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry nitrogen and ethylene. The reactor was dried and degassed at 160°C. Isobutane (400 mL) was added as a diluent and 0.7 mL of a 25 weight percent trioctyl aluminum solution in hexane was added as a scavenger using a gas tight syringe. The reactor was heated to 90°C. 0.200 g of finished catalyst A was added with ethylene pressure and the reactor was pressurized with 143 psi (986 kPa) of ethylene. The polymerization was continued for 40 minutes while maintaining the reactor at 90°C and 143 psi (986 kPa) by constant ethylene flow. The reaction was stopped by rapid cooling and vented. 10.5 g of polyethylene was obtained (Flow Index (FI) = no flow, activity = 209 g polyethylene/mmol catalyst•atm•h).

Example Section II - Example 2 Slurry-Phase Ethylene Polymerization with Catalyst B

Polymerization was performed in the slurry-phase in a 1-liter autoclave reactor equipped with a mechanical stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry nitrogen and ethylene. The reactor was dried and degassed at 160°C. Isobutane (400 mL) was added as a diluent and 0.7 mL of a 25 weight percent trioctyl aluminum solution in hexane was added as a scavenger using a gas tight syringe. The reactor was heated to 90°C. 0.100 g of finished catalyst B was added with ethylene pressure and the reactor was pressurized with 144 psi (993 kPa) of ethylene. The polymerization was continued for 30 minutes while maintaining the reactor at 90°C and 144 psi (993 kPa) by constant ethylene flow. The reaction was stopped by rapid cooling and

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vented. 11.8 g of polyethylene was obtained (FI = no flow, activity = 641 g polyethylene/mmol catalyst•atm•h).

From the data presented above under similar conditions the Group 15 containing metal catalyst compound having the substituted hydrocarbon leaving group, preferably the alkyl substituted with an aryl group of the invention has a much higher productivity than the same compound having a halogen.

The examples in Example Section III, below, utilize of a catalyst system which includes a Silica Bound Aluminum activator.

Example Section III. Catalyst System including Silica Bound Aluminum

The [(2,4,6-Me₃C₆H₂)NHCH₂CH₂]₂NH (Ligand), and the {[(2,4,6-Me₃C₆H₂)NCH₂CH₂]₂NH}Zr(CH₂Ph)₂ (Zr-HN3) were prepared as described in Example Section I.

Preparation of Silica Bound Aluminum (Si-O-Al(C₆F₅)₂)

A sample of 40.686 g of silica (Davison 948, calcined at 600 °C, available from W.R. Grace, Davison Division, Baltimore, Maryland) was slurried in 300 mL of toluene in a 500 mL round bottom flask. Solid Al(C₆F₅)₃•toluene (15.470 g, 24.90 mmol) was added and the mixture stirred for 30 minutes. The mixture was allowed to stand for 18 hours. The silica bound aluminum was isolated by filtration and dried for 6 hours under vacuum with a yield of 49.211 g. Al(C₆F₅)₃•toluene was prepared in accordance with method of described in EP 0 694 548 A1, which is fully incorporated herein by reference.

Preparation of Catalyst A (for purposes of this Example Section III)

To 1.000 g of silica bound aluminum (from Example 4 above) in 20 mL of toluene was added Zr-HN3 (0.076 g, 0.124 mmol) in 5 mL of toluene. The mixture was stirred for 30 minutes. The silica turned orange-red from colorless. The silica was isolated by filtration and dried under vacuum for 6 hours with a yield of 1.051 g. The final transition metal loading was 116 µmol/g, transition metal to silica bound aluminum.

Example Section III - Example 1 Slurry-Phase Ethylene-Hexene Polymerization with Catalyst A

Polymerization was performed in the slurry-phase in a 1-liter autoclave reactor equipped with a mechanical stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry nitrogen and ethylene. The reactor was
5 dried and degassed at 160°C. Isobutane (400 mL) is added as a diluent, 35 mL of 1-hexene, and 0.7 mL of a 25 weight percent trioctyl aluminum in hexane is added as a scavenger using a gas tight syringe. The reactor was heated to 60°C. 0.100 g of finished Catalyst A was added with ethylene pressure and the reactor was pressurized with 78 psi (538 kPa) of
10 ethylene. The polymerization was continued for 30 minutes while maintaining the reactor at 60°C and 78 psi (538 kPa) by constant ethylene flow. The reaction was stopped by rapid cooling and vented. 70.0 g of copolymer was obtained (Flow Index (FI) = no flow, activity = 2320 g polyethylene/mmol catalyst•atm•h, 10.5 weight percent 1-hexene incorporation).

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The examples in Example Section IV, below, utilizes a solution feed of a Group 15 containing metal catalyst.

Example Section IV Solution Feed of Group 15 Containing Metal Catalyst

5

The [(2,4,6-Me₃C₆H₂)NHCH₂CH₂]₂ (NH ligand or pre-Compound I) and the {[(2,4,6-Me₃C₆H₂)NCH₂CH₂]₂NH}Zr(CH₂Ph)₂ (Compound I) were prepared as described in Example Section I.

Preparation of Catalyst A (for purposes of this Example Section IV)

10 **(1.5 wt % in Toluene)**

Note: All procedures below were performed in a glove box.

1. Weighed out 100 grams of purified toluene into a 1 L Erlenmeyer flask equipped with a Teflon coated stir bar.
2. Added 7.28 grams of Tetrabenzyl Zirconium.
- 15 3. Placed solution on agitator and stirred for 5 minutes. All of the solids went into solution.
4. Added 5.42 grams of Compound I.
5. Added an additional 551 grams of purified toluene and allowed mixture to stir for 15 minutes. No solids remained in the solution.
- 20 6. Poured catalyst solution into a clean, purged 1-L Whitey sample cylinder, labeled, removed from glovebox and placed in holding area for operations.

Example Section IV - Example 1

- 25 An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18 kg/hr), hexene was fed to the reactor at a rate of about 0.6 pounds per hour (0.3 kg/hr) and hydrogen was fed to the reactor at a rate of 5 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 27 PPH. The

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reactor was equipped with a plenum having about 1,900 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.041 inch (0.11 cm) hole size was positioned in the plenum gas flow. A solution of 1 wt % Catalyst A in toluene and co-catalyst (MMAO-3A, 1 wt % Aluminum in hexane, (MMAO 3A is modified methyl alumoxane in heptane commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number US 5,041,584)) were mixed in line prior to passing through the injection nozzle into the fluidized bed. The MMAO and catalyst were controlled so that the Al:Zr molar ratio was 400:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 0.28 dg/min (I_{21}) and 0.935 g/cc properties was obtained. A residual zirconium of 1.63 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 2:

An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18 kg/hr), hexene was fed to the reactor at a rate of about 3.5 pounds per hour (1.6 kg/hr) and hydrogen was fed to the reactor at a rate of 25 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 20 PPH. The reactor was equipped with a plenum having about 1,900 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.041 inch (0.11 cm) hole size was positioned in the plenum gas flow. A solution of 1 wt % Catalyst A in toluene, 0.22 PPH of 1-hexene and co-catalyst (MMAO-3A, 4 wt % Aluminum in isopentane) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 746:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 1.2 dg/min (I_2), 29.7 dg/min (I_{21}), 23.9 I_{21}/I_2 ratio and

0.9165 g/cc properties was obtained. A residual zirconium of 0.89 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 3:

5 An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 105° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18 kg/hr), hexene was fed to the reactor at a rate of about 0.6 pounds per hour (0.3 kg/hr) and hydrogen was fed to the reactor at a rate of 6 mPPH. Nitrogen was fed to the
10 reactor as a make-up gas at about 5-8 PPH. The production rate was about 24 PPH. The reactor was equipped with a plenum having about 1,600 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.055 inch (0.14 cm) hole size was positioned in the plenum gas flow. A solution of 1.5 wt % Catalyst A in toluene, and
15 cocatalyst (MMAO-3A, 1.8 wt % Aluminum in 25 % heptane / 75% hexane solution) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 320:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A
20 unimodal polymer having nominal 0.67 dg/min (I_{21}) and 0.9358 g/cc properties was obtained. A residual zirconium of 2.33 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 4:

25 An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 36 pounds per hour (16.3 kg/hr), hexene was fed to the reactor at a rate of about 3.5 pounds per hour (1.6 kg/hr) and hydrogen was fed to the reactor at a rate of 28 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 18 PPH. The
30 reactor was equipped with a plenum having about 1,900 PPH of recycle gas flow. (The

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plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.041 inch (0.11 cm) hole size was position in the plenum gas flow. A solution of 1 wt % Catalyst A in toluene, 0.22 PPH of 1-hexene and cocatalyst (MMAO-3A, 4 wt % Aluminum in isopentane) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 925:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 1.7 dg/min (I_2), 41.7 dg/min (I_{21}), 24.1 I_{21}/I_2 and 0.917 g/cc properties was obtained. A residual zirconium of 0.94 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 5:

An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18 kg/hr), hexene was fed to the reactor at a rate of about 0.6 pounds per hour (0.3 kg/hr) and hydrogen was fed to the reactor at a rate of 3.5 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 22 PPH. The reactor was equipped with a plenum having about 1,500 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.041 inch (0.11 cm) hole size was position in the plenum gas flow. A solution of 1 wt % Catalyst A in toluene and cocatalyst (MMAO-3A, 1 wt % Aluminum in hexane) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 450:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 0.10 dg/min (I_{21}) and 0.931 g/cc properties was obtained. A residual zirconium of 1.36 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 6:

An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18 kg/hr), hexene was fed to the reactor at a rate of about 0.5 pounds per hour (0.23 kg/hr) and hydrogen was fed to the reactor at a rate of 4 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 20 PPH. The reactor was equipped with a plenum having about 2,050 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.041 inch (0.11 cm) hole size was position in the plenum gas flow. A solution of 1 wt % Catalyst A in toluene and cocatalyst (MMAO-3A, 4 wt % Aluminum in isopentane) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 1550:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 0.36 dg/min (I_{21}) and 0.943 g/cc properties was obtained. A residual zirconium of 2.5 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 7:

An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18 kg/hr), hexene was fed to the reactor at a rate of about 0.6 pounds per hour (0.3 kg/hr) and hydrogen was fed to the reactor at a rate of 12 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 20 PPH. The reactor was equipped with a plenum having about 2,050 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.041 inch (0.11 cm) hole size was position in the plenum gas flow. A solution of 1 wt % Catalyst A in toluene and cocatalyst (MMAO-3A, 4 wt % Aluminum in isopentane) were mixed in line prior to

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passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 868:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 3.5 dg/min (I_{21}), 0.115 dg/min (I_2), 30.2 I_{21}/I_2 ratio and 0.949 g/cc properties was obtained. A residual zirconium of 2.5 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 8:

An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 40 pounds per hour (18 kg/hr), hexene was fed to the reactor at a rate of about 1.1 pounds per hour and hydrogen was fed to the reactor at a rate of 12 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 25 PPH. The reactor was equipped with a plenum having about 1,900 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.041 inch (0.11 cm) hole size was positioned in the plenum gas flow. A solution of 1 wt % Catalyst A in toluene and cocatalyst (MMAO-3A, 4 wt % Aluminum in isopentane) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 842:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 41.2 dg/min (I_{21}), 1.22 dg/min (I_2), 33.8 I_{21}/I_2 ratio and 0.940 g/cc properties was obtained. A residual zirconium of 2.77 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 9:

An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 90° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 48 pounds per hour, hexene was fed to the reactor at a rate of about 0.6 pounds per hour (0.3 kg/hr) and

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hydrogen was fed to the reactor at a rate of 10 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 23 PPH. The reactor was equipped with a plenum having about 1,600 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.055 inch (1.4 cm) hole size was position in the plenum gas flow. A solution of 1.5 wt % Catalyst A in toluene, and cocatalyst (MMAO-3A, 1.8 wt % Aluminum in 25%heptane/75%hexane) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 265:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 0.3 dg/min (I_{21}) and 0.933 g/cc properties was obtained. A residual zirconium of 2.38 ppmw was calculated based on a reactor mass balance.

Example Section IV - Example 10:

15 An ethylene hexene copolymer was produced in a 14-inch (35.6 cm) pilot plant scale gas phase reactor operating at 95° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. Ethylene was fed to the reactor at a rate of about 45 pounds per hour, hexene was fed to the reactor at a rate of about 0.6 pounds per hour (0.3 kg/hr) and hydrogen was fed to the reactor at a rate of 6 mPPH. Nitrogen was fed to the reactor as a make-up gas at about 5-8 PPH. The production rate was about 25 PPH. The reactor was equipped with a plenum having about 1,600 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.055 inch (1.4 cm) hole size was position in the plenum gas flow. A solution of 1.5 wt % Catalyst A in toluene, and cocatalyst (MMAO-3A, 1.8 wt % Aluminum in 25 %heptane/75% hexane) were mixed in line prior to passing through the injection nozzle into the fluidized bed. MMAO and catalyst were controlled so that the Al:Zr molar ratio was 350:1. Nitrogen and isopentane were also fed to the injection nozzle as needed to maintain a stable average particle size. A unimodal polymer having nominal 0.4 dg/min (I_{21}) and 0.934 g/cc properties was obtained. A residual zirconium of 2.27 ppmw was calculated based on a reactor mass balance.

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The data for Example Section IV Examples 1 to 10 are summarized in Table II.

Table II

EXAMPLE	Temp. °C	H ₂ /C ₂	C ₆ /C ₂	I ₂ dg/min	I ₂₁ dg/min	Density g/cc	Residual Zr Ppmw
1	85	0.0015	0.0043	N/a	0.28	0.935	1.63
2	85	0.008	0.0410	1.2	29.7	0.9165	0.89
3	105	0.0015	0.0050	N/a	0.67	0.9358	2.33
4	85	0.0087	0.0405	1.7	41.7	0.917	0.94
5	85	0.0006	0.0051	N/a	0.1	0.931	1.36
6	85	0.0023	0.0012	N/a	0.36	0.943	2.50
7	85	0.0051	0.0013	0.115	3.5	0.949	2.50
8	85	0.0114	0.0154	1.22	41.2	0.940	2.77
9	90	0.0015	0.0050	N/a	0.3	0.933	2.38
10	95	0.0015	0.0050	N/a	0.4	0.934	2.27

Example Section IV - Example 11:

300 pounds (138 kg) of polyethylene produced according to example 4 above (referred to as Polymer A) was compounded on a Werner-Fleiderer ZSK-30 twin screw extruder with 1000 ppm Irganox™ 1076 and 1500 ppm Irgafos™ 1068 at a melt temperature of 200°C and formed into pellets. Then the pellets were blown into a 1.0 mil (25 µm) film on an Gloucester blown film extrusion line at 188 lb/hr (85 kg/hr) rate, at 390°F (199°C) melt temperature, 24 inch (61cm) frostline height, 2.5 blow-up ratio, and 60 mil (1524 µm) die gap. ESCORENE™ HD7755.10 (a conventional series reactor product of Exxon Chemical Company in Mt. Belvue Texas) was run at the same conditions as a comparison. All films were conditioned according to 23°C, 50% humidity for 40 hours. The data are presented in Tables III and IV.

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Table III

Example	Escorene™ LL3002.32	Polymer A 1.8 g/10min MI	Escorene™ LL3001.63
I ₂ , g/ 10 min	2	1076	1
I ₂₁ /I ₂	29	24	27
Pellet density g/cc	0.918	0.918	0.918
Head Pressure psi (MPa)	2690 (19)	2470 (17)	3380 (23)
Motor load, %	43	31.2	50.4
Film gage mil, (μm)	1 (25)	1 (25)	1 (25)
Film Density, g/cc	0.917	0.916	0.917
26 inch (66 cm) Dart, g	136	168	149
Elm. Tear g/mil (g/μm) MD	310(12.7)	254(10.4)	223(9.1)
Elm. Tear g/mil (g/μm) TD	609(24.9)	630(25.7)	753(30.7)
1% Secant Mod. psi (MPa) MD	30430 (210)	31580 (218)	31320 (216)
1% Secant Mod. psi (MPa) TD	38950 (269)	42120 (290)	39750 (274)
Ult. Tensile Str. psi (MPa) MD	7444 (51)	8551 (59)	8880 (61)
Ult. Tensile Str. psi (MPa) TD	6498 (45)	9892 (68)	6894 (48)
Ultimate Elongation % MD	641	546	552
Ultimate Elongation % TD	793	694	756
45° gloss	40	79	23
Haze %	22	4.4	20

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Table IV

Example	Polymer A 1.3 MI	EXCEED™ 350D60
I ₂ , g/ 10 min	1.35	1
I ₂₁ /I ₂	23	16
Pellet density g/cc	0.918	0.918
Head Pressure psi (MPa)	3010 (21)	3810 (26)
Motor load, %	37.2	56.7
Film gage mil, (μm)	1 (25)	1 (25)
Film Density, g/cc	0.916	0.916
26 inch (66 cm) Dart, g	276	646
Elm. Tear g/mil (g/μm) MD	219?	264?
Elm. Tear g/mil (g/μm) TD	616?	392?
1% Secant Mod. psi (Mpa) MD	31100 (214)	29040 (200)
1% Secant Mod. psi (Mpa) TD	41470 (286)	33050 (228)
Ult. Tensile Str. psi(MPa) MD	9017 (62)	9986 (69)
Ult. Tensile Str. psi (Mpa) TD	7684 (53)	8535 (59)
Ultimate Elongation % MD	529	504
Ultimate Elongation % TD	690	646
45° gloss	74	25
Haze %	5	23

na = not available

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The examples in Example Section V, below, utilizes solution feed of a mixed catalyst system which includes a Group 15 containing metal catalyst and a bulky ligand Metallocene Catalyst.

5 **Example Section V. Solution Feed of Mixed Catalyst Systems Including Group 15**
Containing Metal Catalyst and Bulky Ligand Metallocene Catalyst

Catalyst 1

10 For purposes of this Example Section V, Catalyst 1 is indenyl zirconium tris pivalate, a bulky ligand metallocene-type compound, prepared as described in Example Section 1.

Preparation of Catalyst 1 - 1 wt% in Hexane Solution

All procedures were performed in a glove box.

- 15 2. Transfer 1 liter of purified hexane into a 1 L Erlenmeyer flask equipped with a Teflon coated stir bar.
5. Add 6.67 grams of indenyl zirconium tris pivalate dried powder.
6. Place solution on magnetic agitator and stir for 15 minutes. All of the solids go into solution.

Pour solution into a clean, purged 1-L Whitey sample cylinder, labeled, and removed from
20 glovebox and place in holding area until use in operation.

Catalyst 2

For purposes of this Example Section V, Catalyst 2 the [(2,4,6-Me₃C₆H₂)NHCH₂CH₂]₂NH ligand (Ligand I) and the {[(2,4,6-Me₃C₆H₂)NCH₂CH₂]₂NH}Zr(CH₂Ph)₂ (Compound I) were prepared as described in
25 Example Section I.

Preparation of Catalyst 2 - 1.5 wt % in Toluene Solution

Note: All procedures below were performed in a glove box.

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8. Weighed out 100 grams of purified toluene into a 1 L Erlenmeyer flask equipped with a Teflon coated stir bar.
9. Added 7.28 grams of Tetrabenzyl Zirconium.
10. Placed solution on agitator and stirred for 5 minutes. All of the solids went into solution.
- 5 11. Added 5.42 grams of Ligand I.
12. Added an additional 551 grams of purified toluene and allowed mixture to stir for 15 minutes. No solids remained in the solution.
13. Poured catalyst solution into a clean, purged 1-L Whitey sample cylinder, labeled, removed from glovebox and placed in holding area for operations.

10

Example Section V - Example 1:

An ethylene hexene copolymer was produced in a 14-inch pilot plant scale gas phase reactor operating at 85° C and 350 psig (2.4 MPa) total reactor pressure having a water cooled heat exchanger. The reactor was equipped with a plenum having about 1,600 PPH of recycle gas flow. (The plenum is a device used to create a particle lean zone in a fluidized bed gas-phase reactor. See US Patent 5,693,727.) A tapered catalyst injection nozzle having a 0.055 inch (1.4 cm) hole size was positioned in the plenum gas flow. Prior to starting the catalyst feed, ethylene pressure was about 220 psia (1.5 MPa), 1-hexene concentration was about 0.3 mol % and hydrogen concentration was about 0.12 mol %.

20

Catalyst 2 was dissolved in a 0.5 wt% solution in toluene and was fed to reactor at 12 cc/hr. MMAO-3A, 1 wt % Aluminum) co-catalyst was mixed with the Catalyst 2 in the feed line prior to the reactor at a molar ratio of 400:1 Al/Zr. The production rate was about 24 lb/hr (10.9 kg/hr). In addition, 5.0 lbs/hr (2.3 kg/hr) Nitrogen and 0.1 lbs/hr (0.05 kg/hr) 1-hexene and 0.2 lb/hr (0.09 kg/hr) isopentane were also fed to the injection nozzle. The polymer had a flow index of 0.31 and a density of 0.935 g/cc. After this was established, the catalyst feed rate was reduced to 6 cc/hr of catalyst 2 and a 0.125 wt% Catalyst 1 in hexane solution feed was added to the injection line at 13 cc/hr. The entire order of addition was the hexene and the MMAO mixed with the Catalyst 1, Catalyst 2 solution was added, then isopentane and nitrogen. The Al/Zr for the entire system was about 500. Within 6 hours of the addition of Catalyst 1, the bimodal polymer had a nominal 12.9 dg/min (I_{21}), a 130

30

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MFR(melt flow ratio I_{21}/I_2)and 0.953 g/cc density. The resin average particle size was 0.0479 inched (0.12 cm). A residual zirconium of 0.7 ppmw was measured by x-ray fluorescence.

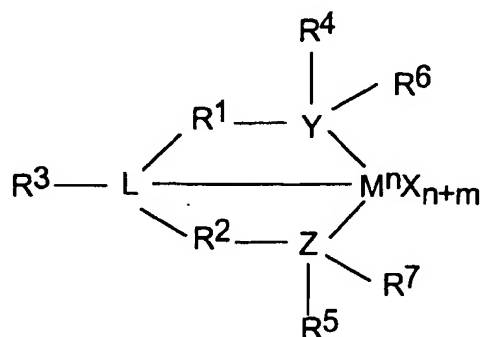
All documents described herein are incorporated by reference herein, including any
5 priority documents and/or testing procedures. As is apparent from the foregoing general
description and the specific embodiments, while forms of the invention have been illustrated
and described, various modifications can be made without departing from the spirit and scope
of the invention. It is within the scope of this invention to use two or more Group 15
containing metal compounds with one or more bulky ligand metallocene catalyst system
10 and/or one or more conventional type catalyst system. Accordingly it is not intended that the
invention be limited thereby.

Claims:

1. A process for polymerizing olefin(s) in the presence of a catalyst system comprising a Group 15 containing metal catalyst compound.
- 5 2. The process of Claim 1 wherein the catalyst system further comprising a bulky ligand metallocene catalyst compound, a conventional transition metal catalyst compound, or a combination thereof.
- 10 3. The process of any one of the preceding claims wherein the Group 15 containing metal catalyst compound is a Group 15 containing bidentate or tridentate ligated Group 3 to 14 metal catalyst compound.
- 15 4. The process of any one of the preceding claims wherein the Group 15 containing hafnium catalyst compound is a Group 3 to 14 metal atom bound to at least one leaving group and to at least two Group 15 atoms, where at least one of the at least two Group 15 atoms is bound to a Group 15 or 16 atom through a bridging group, preferably where the bridging group is selected from the group consisting of a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead, and phosphorus.
- 20 5. The process of claim 4 wherein the Group 15 or 16 atom may also be bound to nothing, a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group, and wherein each of the two Group 15 atoms are also bound to a cyclic group and may optionally be bound to hydrogen, a halogen, a heteroatom or a hydrocarbyl
- 25 group, or a heteroatom containing group.

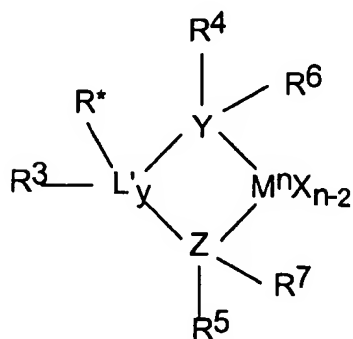
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6. The process of any one of the preceding claims wherein the Group 15 containing metal compound is represented by the formulae:



Formula (I)

or



Formula (II)

wherein M is a Group 3 to 14 metal, preferably a Group 3 to 7 metal and more preferably a Group 4 to 6 metal;

each X is independently a leaving group;

10 y is 0 or 1;

n is the oxidation state of M;

m is the formal charge of the YZL or the YZL' ligand;

L is a Group 15 or 16 element;

L' is a Group 15 or 16 element or Group 14 containing group;

15 Y is a Group 15 element;

Z is a Group 15 element;

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R^1 and R^2 are independently a C_1 to C_{20} hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus;

R^3 is absent or a hydrocarbon group, hydrogen, a halogen, a heteroatom containing group;

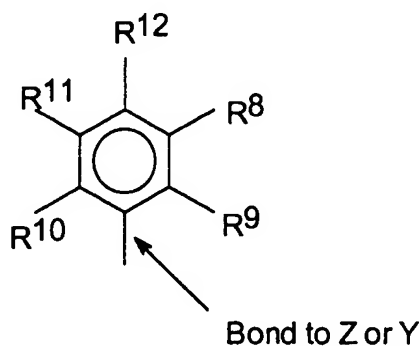
R^4 and R^5 are independently an alkyl group, an aryl group, substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic arylalkyl group, a substituted cyclic arylalkyl group or multiple ring system;

R^1 and R^2 may be interconnected to each other, and/or R^4 and R^5 may be interconnected to each other;

R^6 and R^7 are independently absent, or hydrogen, an alkyl group, halogen, heteroatom or a hydrocarbyl group; and

R^* is absent, or is hydrogen, a Group 14 atom containing group, a halogen, a heteroatom containing group.

7. The process of claim 6 wherein R^4 and R^5 are represented by the formula:



wherein R^8 to R^{12} are each independently hydrogen, a C_1 to C_{40} alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms, preferably a C_1 to C_{20} linear or branched alkyl group, preferably a methyl, ethyl, propyl or butyl group, any two R groups form a cyclic group and/or a heterocyclic group. The cyclic groups may be aromatic.

8. The process of claim 7 wherein R^9 , R^{10} and R^{12} are independently a methyl, ethyl, propyl or butyl group, or wherein R^9 , R^{10} and R^{12} are methyl groups, and R^8 and R^{11} are hydrogen.

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9. The process of any one of the preceding claims 6 to 8, wherein L, Y, and Z are independently nitrogen, R¹ and R² are a hydrocarbon radical, R³ is hydrogen, and R⁶ and R⁷ are absent, or wherein L and Z are independently nitrogen, L' is a hydrocarbonyl radical, and R⁶ and R⁷ are absent.

5

10. The process of any one of the preceding claims wherein the Group 15 containing metal catalyst compound contains at least one substituted hydrocarbon leaving group having 6 or greater carbon atoms, and preferably where the at least one substituted hydrocarbon leaving group is an aryl substituted alkyl group, and most preferably where the aryl substituted alkyl group is benzyl.

10

11. The process of any of the preceding claims wherein the catalysts system further comprises an activator(s).

15

12. The process of any one of the preceding claims wherein the catalyst compound(s) and/or the activator compound(s) are introduced, into a gas or slurry phase reactor, in a liquid carrier.

20

13. The process of claim 12 utilizing a gas phase reactor wherein at least two catalysts and at least one activator are introduced into the reactor in the liquid carrier, wherein each catalyst is activated independently and the catalysts and the activator(s) are combined in the liquid carrier before being introduced into the reactor.

25

14. The process of claim 13 wherein the catalysts are activated sequentially.

15. The process of claim 13 wherein

i) the catalysts are combined in a liquid carrier and thereafter the activator(s) is introduced into the liquid carrier;

or wherein

30

ii) the catalysts are combined in a liquid carrier then introduced into a channeling means connecting to the reactor and thereafter the activator(s) is introduced into the channeling means at the same or different point as the catalysts.

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16. The process of claims 12 to 15 wherein the liquid carrier containing the catalyst(s) and the activator(s) is placed into an apparatus for introducing the liquid carrier into the reactor.

5

17. The process of claim 16 wherein the catalysts and liquid carrier are introduced into the apparatus before the activator is introduced into the apparatus.

18. The process of claims 12 or 17 wherein the liquid carrier comprises a liquid stream
10 flowing or sprayed into the reactor.

19. The process of claims 12 to 18 wherein at least one catalyst, at least one activator and the liquid carrier are placed into an apparatus for introduction into the reactor wherein additional catalyst(s) is/are introduced into the apparatus after the first catalyst and activator
15 are introduced into the apparatus.

20. The process of claim 12 wherein

i) a first combination comprising at least one catalyst in a liquid carrier is introduced into an apparatus connecting to the reactor, and a second composition comprising
20 at least one activator in a liquid carrier is introduced into the apparatus connecting to the reactor, then, after a period of time, a different catalyst in a liquid carrier is introduced into the apparatus connecting to the reactor, and then the catalyst-activator combination is introduced into the reactor;
or wherein

25 ii) at least one catalyst(a) and at least one activator(a) are combined in a liquid carrier, and at least one catalyst(b) and at least one activator(b) are combined in a liquid carrier, wherein the catalyst(b) is different from the catalyst(a) and/or the activator (b) is different from the activator(a), and thereafter both combinations are introduced into an apparatus connecting to the reactor, and, thereafter the combinations are introduced into
30 the reactor;
or wherein

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iii) the liquid carrier containing catalyst(b) and activator(b) is introduced into the apparatus connecting to the reactor after the liquid carrier containing catalyst(a) and activator(a) is introduced into the apparatus connecting to the reactor;
or wherein

5 iv) a first composition comprising at least one catalyst(a), at least one activator(a) and a liquid carrier is placed in an apparatus connected to the reactor, and a second composition comprising at least one catalyst(b), at least one activator(b) and a liquid carrier, wherein the catalyst(b) and/or the activator (b) is different from the catalyst(a) and/or the activator(a), is introduced into the apparatus connecting to the reactor after the first
10 composition is, and thereafter the combined compositions is introduced into the reactor;
or wherein

v) at least one catalyst and the liquid carrier are placed into an apparatus for introduction into the reactor wherein additional catalyst(s) and activator(s) are introduced into the apparatus after the first catalyst is introduced into the apparatus;
15 or wherein

vi) a first composition comprising at least one catalyst(a), at least one activator(a) and a liquid carrier is introduced into an apparatus feeding into a reactor, and thereafter a second catalyst in a liquid carrier is added to the apparatus feeding into the reactor, and thereafter a second activator in a liquid carrier is added to the apparatus feeding into the reactor, and
20 thereafter the total combination is introduced into the reactor.

21. The process of claim 12 wherein the catalyst compound(s) and/or the activator(s) are combined before being placed in the liquid carrier, and/or wherein the carrier is an alkane, preferably pentane, hexane, and/or isopentane.

25

22. The process of any one of the preceding claims 1 to 11 wherein the catalyst compound(s) and/or the activator compound(s) is supported on a carrier(s).

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23. The process of claim 22 wherein the activator comprises alkyl aluminum compounds, alumoxanes, modified alumoxanes, non-coordinating anions, boranes, borates ionizing compounds and/or a Lewis acid aluminum containing activator described by the formula:



5 where R is a monoanionic ligand;

ArHal is a halogenated C₆ aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together; and

n = 1 to 2, preferably n=1.

10 24. The process of any one of the preceding claims wherein the process is selected from the group consisting of a continuous gas phase process and a continuous slurry phase process.

15 25. The process of any of the preceding claims wherein the olefin(s) is ethylene, or propylene, or ethylene and at least one other monomer having from 3 to 20 carbon atoms.

26. A catalyst system comprising a Group 15 containing metal catalyst compound an activator, and optionally a carrier.

20 27. The catalyst system of claim 26 further comprising a bulky ligand metallocene catalyst compound, a conventional transition metal catalyst compound or a combination thereof.

25 28. The catalyst system of claim 26 or 27 wherein the Group 15 containing metal catalyst compound is a Group 15 containing bidentate or tridentate ligated Group 3 to 14 metal catalyst compound.

30 29. The catalyst system of claim 26 to 28 wherein the Group 15 containing hafnium catalyst compound and the bulky ligand metallocene catalyst compound, if present, are contacted with the activator to form a reaction product that is then contacted with the carrier.

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30. The catalyst system of claims 26 to 29 wherein the system is supported on a carrier and the activator is a Lewis acid aluminum containing activator described by the formula:



where R is a monoanionic ligand;

ArHal is a halogenated C₆ aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together; and
n = 1 to 2, preferably n=1.

31. Use of a Group 15 containing Group 3 to 14 metal catalyst compound to produce a high molecular weight component in a multimodal polymer composition.

32. Use of a bulky ligand metallocene catalyst compound to produce a low molecular weight component in a multimodal polymer composition.

33. The process of claim 2 wherein the bulky ligand metallocene compound is of the general formula $L^D M Q_2(YZ)X_n$

wherein M is a Group 3 to 16 metal, preferably a Group 4 to 6 metal,

L^D is a bulky ligand that is bonded to M, preferably an indenyl or fluorenyl

group,

each Q is a univalent anionic ligand bonded to M.

$Q_2(YZ)$ forms a uncharged polydentate ligand;

X is a univalent anionic group when n is 2 or X is a divalent anionic group when n is 1, and

n is 1 or 2.

34. The process of claim 33 wherein X is a carbamate, carboxylate, or other heteroallyl moiety described by the QYZ combination.

35. The process of claims 2 and 33 wherein the Group 15 containing metal compound to the bulky ligand metallocene type compound are present in a molar ratio of 1:99 to 99:1, preferably in a molar ratio of 20:80 to 80:20.

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36. A polymer produced by the process of claims 2 and 33 to 35 wherein the polymer has a density of about 0.89 to 0.97 g/cm³, and/or I₂₁ of about 1 to 10dg/min or less, and/or an I₂ of about 0.01 to 1000dg/min, and/or an I₂₁/I₂ of 80 or more, and/or a M_w of 180,000 or more, and/or an ash content of less than 100ppm, and/or contains a nitrogen containing ligand
5 detectable by High Resolution Mass Spectrometry.

37. An ethylene based polymer composition produced in a single reactor with at least two catalysts, an I₂₁/I₂ greater than 80, and an ash content of less than 100ppm, and/or has density of the polyethylene is 0.945 g/cm³ or more.

10 38. The composition of claim 37 wherein the polymer has an extrusion rate of greater than about 17lbs/hour/inch (2.8 Kg/hour/cm) of die circumference.

39. The composition of claim 37 that when formed into a film of 0.5 mil (13μ) thickness
15 has haze of 60% or less and a 45° gloss of 13 or more, wherein the film is a blown film or a cast film, and/or wherein film preferably has an MD Tear of .5mil (13μ) film of between about 5g/mil (0.20 g/μ) and 25g/mil (1.0 g/μ).

40. An ethylene polymer or copolymer having a residual metal content of 2.0 ppm
20 zirconium or less, an I₂₁ less than or equal to 12, an I₂₁/I₂ greater than or equal to 80, and/or a residual nitrogen content of 2.0 ppm or less, and/or an ash content of less than 100 ppm.

41. A film comprising extruding, blowing or casting a film from polymer produced by the process of claim 12.

25 42. A composition comprising polyethylene produced by the process of claim 12 having a density of 0.910 g/cc to 0.935 g/cc and a melt index of 10 dg/min or less, a haze of 10% or less and a 45° gloss of 60 units or more.

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43. The composition of claim 42 wherein the polyethylene has a density of 0.915-0.930 g/cc, and/or has a melt index of 5 dg/min or less, and/or a haze of 7% or less, and/or a 45° gloss of 75 units or more, and/or a dart impact of 150g or more (as measured by ASTM D 1709 Method A), and/or an Elmendorf tear of 100 g or more in the machine direction, and/or
5 an Elmendorf tear of 500g or more in the transverse direction.

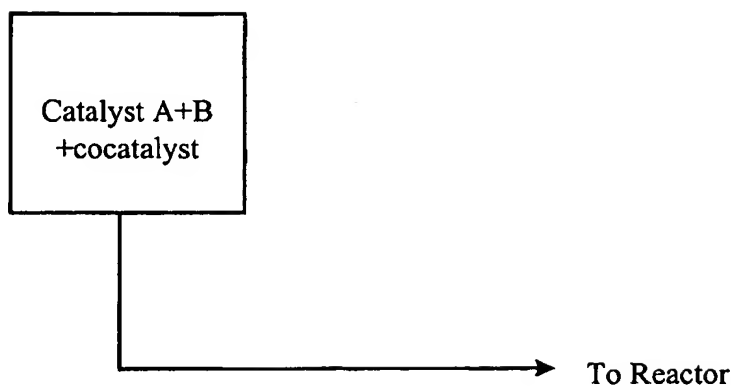
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Figure 1.

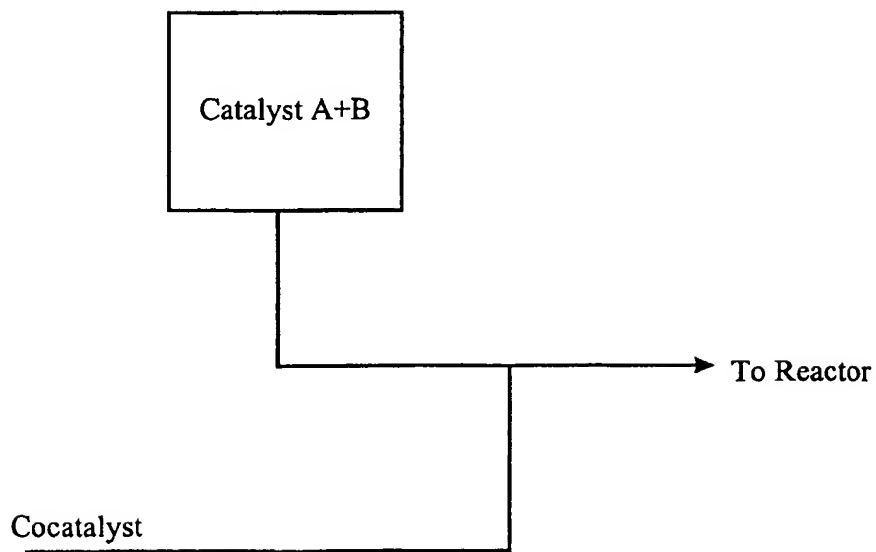


Figure 2.

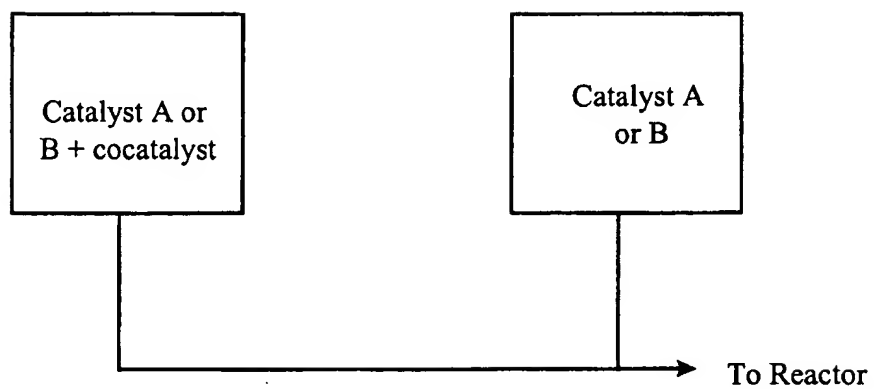
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Figure 3.

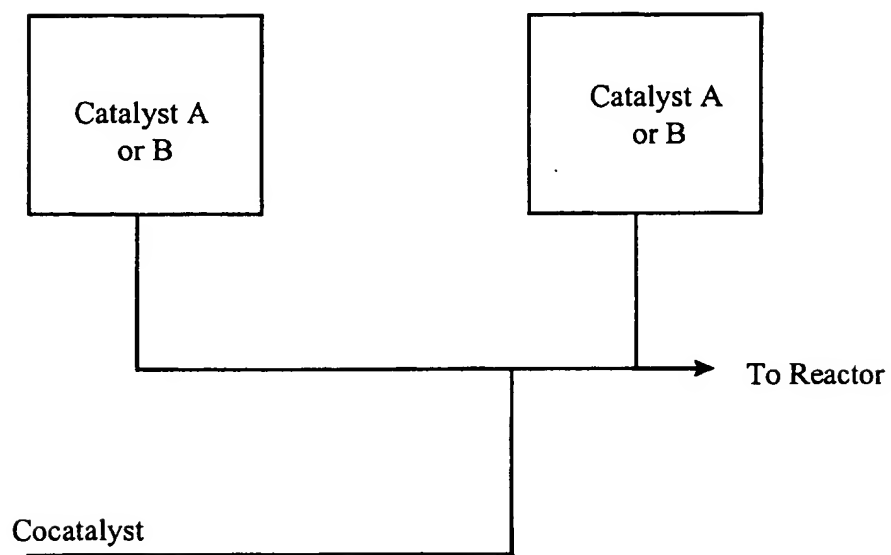


Figure 4.

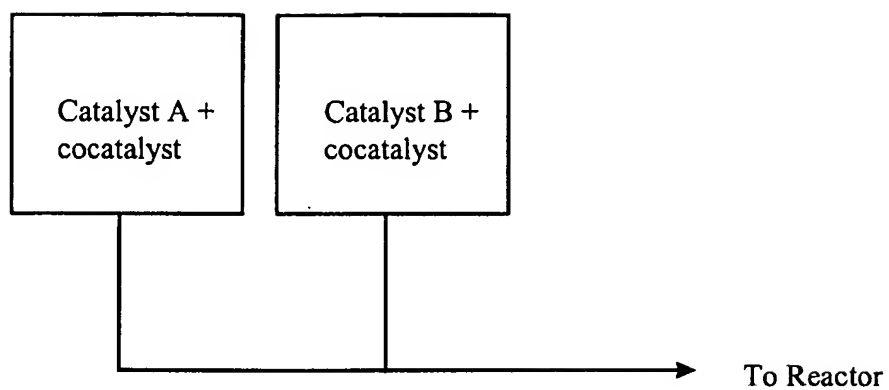
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Figure 5.

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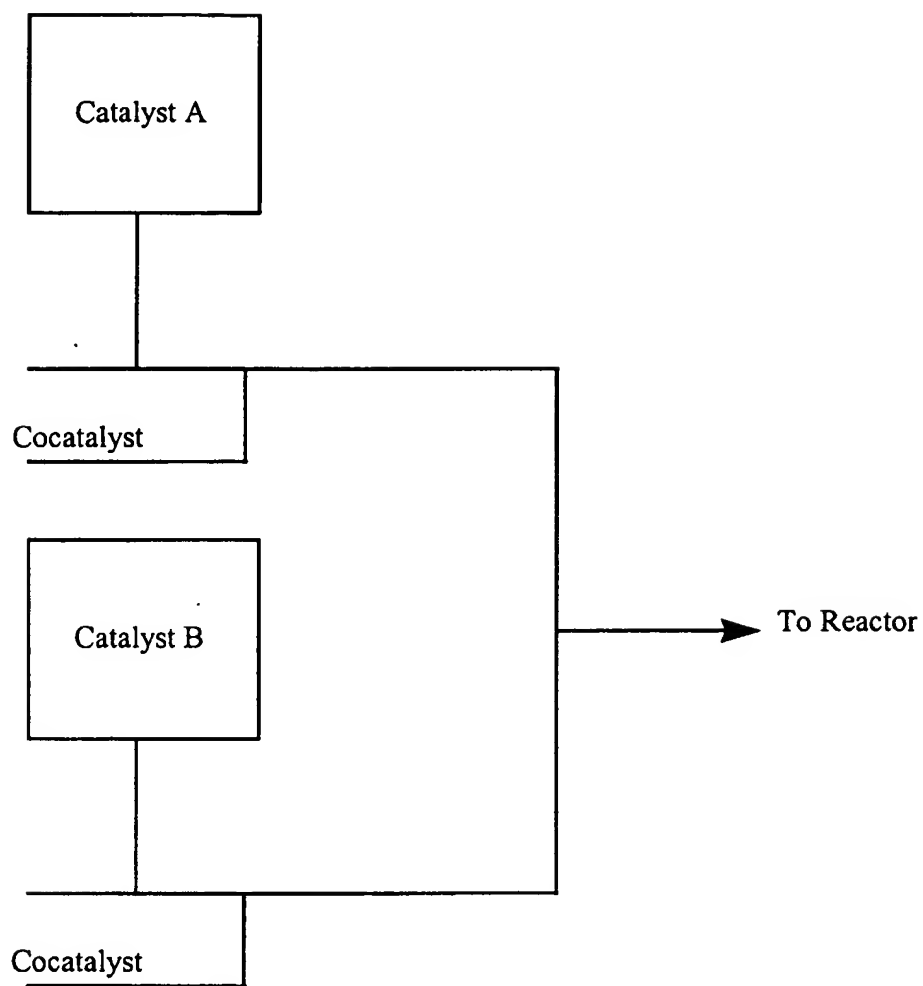


Figure 6.

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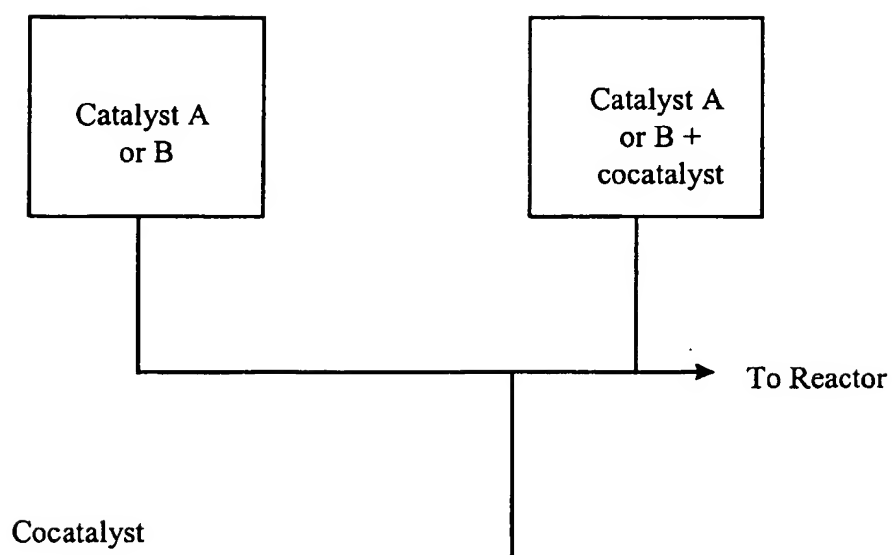


Figure 7.

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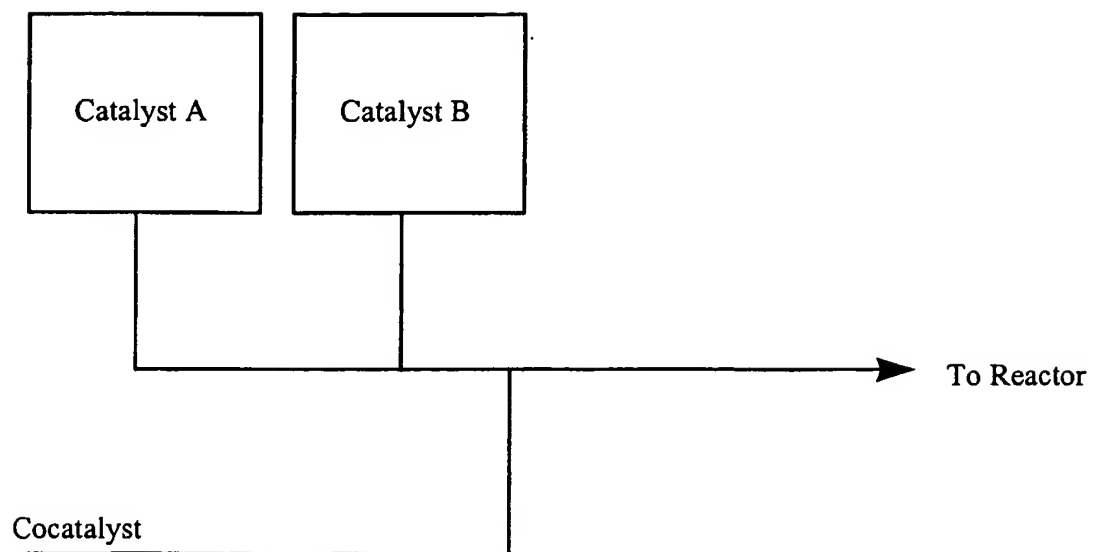


Figure 8.

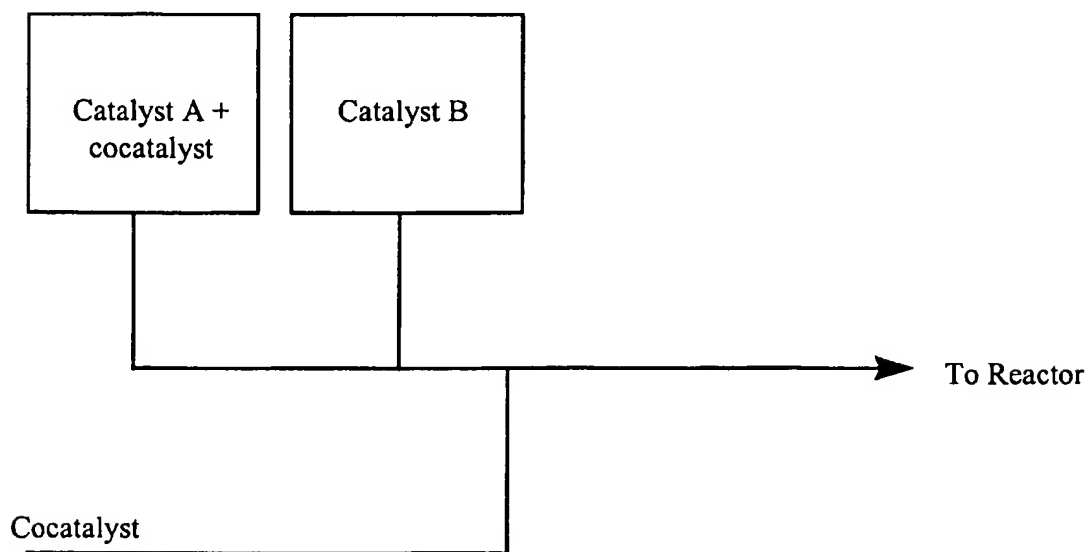


Figure 9.

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/US 00/13313

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/00 C08F10/02 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 874 005 A (MITSUI CHEMICALS INC) 28 October 1998 (1998-10-28) cited in the application the whole document ---	1-43
X	EP 0 893 454 A (MITSUI CHEMICALS INC) 27 January 1999 (1999-01-27) cited in the application the whole document ---	1-43
X	WO 98 37106 A (EXXON CHEMICAL PATENTS INC) 27 August 1998 (1998-08-27) the whole document ---	1-43
X	WO 99 01460 A (UNION CARBIDE CHEM PLASTIC) 14 January 1999 (1999-01-14) the whole document ---	1-43
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

28 November 2000

Date of mailing of the international search report

04/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Golde, L

INTERNATIONAL SEARCH REPORT

Intern: al Application No

PCT/US 00/13313

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 46303 A (KIMBERLEY BRIAN STEPHEN ;SAMSON JOHN NORMAN REID (GB); BP CHEM INT) 16 September 1999 (1999-09-16) the whole document -----	1-43
X	WO 99 46304 A (KIMBERLEY BRIAN STEPHEN ;PRATT DAVID (GB); BP CHEM INT LTD (GB)) 16 September 1999 (1999-09-16) the whole document -----	1-43

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